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METHODS FOR DETERMINING THE HYDROGEN-ION CONCENTRATION OF SOILS

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By E. F. Snyder, *associate chemist, Division of Soil Fertility, Soil Investigations, Bureau of Chemistry and Soils*

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REVIEW OF LITERATURE

Hydrogen-electrode and colorimetric methods for the determination of the hydrogen-ion exponents of soils were published in 1916 by Gillespie (*46*),[1] and the occurrence of truly acid soils was demonstrated. This first comparison of two different methods, the results of which showed substantial agreement, was of fundamental importance. Sharp and Hoagland (*93*) subsequently published a hydrogen-electrode procedure for the determination of the hydrogen-ion concentration of soils, together with a discussion of several phases of acidity and absorption. Few earlier electrometric measurements of this intensity factor of acidity in soils had been published. In this connection may be mentioned some earlier electrometric measurements by Saidel (*91*), limited to boiled alkaline extracts, and by Fischer (*41*), whose measurements were made with the hydrogen electrode. In order to obtain constant potentials, however, Fischer (*41*) was obliged to continue his observations for 7 or 8 hours.

[1] Italic numbers in parentheses refer to literature cited, p. 41.

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PHYSICOCHEMICAL ACIDITY AND THE pH VALUE

Preliminary to considering the methods, it may be well to discuss briefly the physicochemical significance of acidity.

Water dissociates into hydrogen ions H^+ and hydroxyl ions OH^-, the former being characteristic of acids and the latter of bases, the reversible reaction being represented as follows:

$$HOH \rightleftarrows H^+ + OH^-$$

According to the law of mass action this reversible reaction at equilibrium is represented by the following equation:

$$\frac{[H^+]\,[OH^-]}{[HOH]} = k$$

Since the molecular concentration of water may be regarded as constant in dilute solutions, the above equation may be written as follows:

$$[H^+]\,[OH^-] = K_w$$

Here K_w is the ionic product, but generally referred to as the dissociation constant of water. The value of K_w, as given by Lewis, Brighton, and Sebastian (*75*) for pure water is $K_w = 1.012 \times 10^{-14}$ at 25° C., which gives a concentration of $[H^+]$ and $[OH^-]$ equal to 1.006×10^{-7}, or approximately 1.00×10^{-7}. In pure water, the concentration of the hydrogen ions is equal to the concentration of the hydroxyl ions, and the resulting condition is one of physicochemical neutrality. This neutral point probably possesses little other physical significance and is seldom the theoretical or even practical point of titrimetric neutrality. Since the product of the concentrations of the two ions is a constant, approximately 1.00×10^{-14} at 25° C., it is apparent that in any solution, whatever the concentration of the hydroxyl ions, there must always be present sufficient hydrogen ions to satisfy the above equation. One may, therefore, refer to any solution, acid or alkaline, in terms of its hydrogen-ion concentration. Instead of expressing the hydrogen-ion concentration as a negative power of 10 there has been introduced by Sörensen (*98*) a pH scale of expression. In the working formula of the hydrogen electrode the potential is related to the logarithm of the reciprocal of the hydrogen-ion concentration $\log \frac{1}{[H^+]}$, and it is to this logarithmic term that the symbol pH is given, thus, $pH = \log \frac{1}{[H^+]}$. Various reasons for this preference of expressing the hydrogen-ion concentration will not be discussed here, as they have been previously given by Clark (*33*).

According to the pH scale, at approximately pH 7 the hydrogen- and hydroxyl-ion concentrations are equal and the condition is one of physicochemical neutrality. Briefly stated, below pH 7, as the pH values decrease, the hydrogen-ion concentration becomes greater than the hydroxyl-ion concentration; and above pH 7, as the pH values increase, the hydrogen-ion concentration becomes less than the hydroxyl-ion concentration. For each unit decrease in pH the hydrogen-ion concentration becomes 10 times each preceding concentration. It is well to bear in mind that the hydrogen-ion exponent

is a measure of the intensity factor of acidity and not of the quantity of acid or acid substances present. The relationship between hydrogen-ion concentrations and pH values is shown in table 1.

TABLE 1.—*Relationship between hydrogen-ion concentrations and pH values*

[H+]	pH	[H+]	pH
10^{-0}	0	10^{-8}	8
10^{-1}	1	10^{-9}	9
10^{-2}	2	10^{-10}	10
10^{-3}	3	10^{-11}	11
10^{-4}	4	10^{-12}	12
10^{-5}	5	10^{-13}	13
10^{-6}	6	10^{-14}	14
10^{-7}	7		

In several instances in the literature investigators have averaged a series of pH values and apparently lost sight of the exponential significance of this term. The arithmetical averaging of pH values and plotting against arithmetical quantities has been referred to by Wherry (*105*).

FACTORS AFFECTING THE HYDROGEN-ION CONCENTRATION OF SOILS

PERIODIC VARIATION OF THE HYDROGEN-ION CONCENTRATION

In studying the hydrogen-ion concentration of soils, the time of sampling is of significance. Lipman and co-workers (*76*) found fluctuations of about 0.7 pH in the surface soils of their check plots from May to November. Results obtained by Kelley (*64*) show that over a period of a year monthly tests reveal a fluctuation in the pH value of a soil amounting at times to a pH of 1 in the subsoil as well as at the surface. From the results of Baver (*10*) it is apparent that the acid soils show a continual increase in hydrogen-ion concentration from May to September, whereas the alkaline soils show no consistent variations during this period. In the case of the acid soils there was a consistent increase in acidity from the spring to the fall, with a return to nearly the original acidity the following spring. From May to September acid soils varied as much as 0.9 pH and alkaline soils about 0.6 pH. The rainfall and season seemed to be two important factors affecting these variations in the soil reaction. The results of Smith and Robertson (*95*) show that the acidity of the uncropped soil increases to a maximum during the growing season and that the change may amount to more than one pH unit. Also the plant reduces the change in acidity to a marked extent and at the height of growth there is a considerable difference between the acidity of the cropped and uncropped soil. At the end of the growing season that difference has practically disappeared and the acidity of the soil approaches the value found at the beginning of the season. According to Hester and Shelton (*57*) lime recommendations made on the basis of the pH value of the soil without knowledge of the seasonal variation would lead to considerable error. The seasonal factor is of special interest on soils with low buffer capacity on which truck crops are grown, according to Hester and Shelton.

In the interpretation of pH data of soils, therefore, the seasonal factor should be considered.

EFFECT OF DRYING OF SOIL ON THE HYDROGEN-ION CONCENTRATION

Results obtained by the writer on the effect of air-drying of soils on the pH value show that air-drying of acid soils slightly lowers the pH value. Burgess (*29*) found that air-drying of acid soils had but little effect on their hydrogen-ion concentration, whereas with slightly alkaline soils it decreases the pH value. This effect was particularly noticeable at a temperature of 103° C. Rost and Fieger (*90*) determined the pH variation resulting from air-drying acid and alkaline soils and found that some samples became more acid and some more alkaline, with a general tendency, however, for the air-dried samples to become more acid than the fresh ones. There was a general tendency for fresh, moist soils to become more acid when stored for 3 months in air-tight glass containers. It was concluded that the only reliable indication of field conditions was obtained with soil samples freshly taken. Results obtained by Healy and Karraker (*54*) show that air-drying acid soils slightly lowered the pH values. Joseph and Martin (*62*) found that oven-drying alkaline soils lowered the pH of the extract, as compared with the extract of the undried soil. Results by Biilmann and Tovborg-Jensen (*20, p. 261*) on 18 soils from about pH 5.2 to 8.3 show the air-dried soils to be slightly more acid than the same soils before air-drying. They state: "Our measurements *only* permit us to conclude that the *air-dried soil samples show pH values which correspond essentially to the values found with non-air-dried samples.*" The work of Baver (*10*) shows that the reaction of acid surface soils is not significantly affected by air-drying, but that there is a considerable decrease in alkalinity with the alkaline soils. The air-drying of subsoils produced a marked increase in acidity, which increased with depth. From the data presented it is evident that fresh samples for hydrogen-ion exponent determinations give a closer expression of soil reaction in the field than do air-dried samples. As stated by Baver, for practical purposes, therefore, it seems that the hydrogen-ion concentration of an air-dried soil is sufficiently accurate, but for refined reaction studies fresh samples should be used. Crowther (*36*) found that air-drying of soil samples generally reduced the pH value slightly (about 0.1) as compared with fresh soils. Oven-drying produced a much greater reduction. Crowther states (*36, p. 206*):

> For special purposes it may be necessary to limit the measurements to freshly taken samples, but, in view of the other empirical factors introduced in making soil suspensions and the difficulties in working with a large series of fresh soils, it was decided to secure comparable conditions in all cases by using air-dried soils.

The mineral soils studied by Coles and Morison (*35*) showed a considerable decrease in pH by heating in a steam oven at 98° C., followed by a slight decrease on further heating. Drying in a desiccator at ordinary temperatures lowered the pH but not as much as drying in an oven at 98°. Bailey (*6*) studied the effect of air-drying on 327 moist horizon samples from 64 representative virgin profiles from widely scattered parts of the United States, Puerto Rico, and Canada. Only 2 of the 64 profiles contained horizons that changed 0.50 pH or more on air-drying. Where the change on drying and storing exceeded 0.10 pH, with only 2 exceptions, it was toward greater acidity.

This is in general agreement with other investigators. The greater part of the profiles studied did not change more than 0.10 pH in any of their horizons on air-drying. Bailey concluded that the determination of the hydrogen-ion concentration should be made on air-dried soils rather than on samples fresh from the field.

The general conclusion seems apparent that drying of soils is, as a rule, accompanied by a change in reaction, generally in the direction of increased acidity. In some instances it may be desirable to know the pH value of the fresh soil sample; however, the air-dried soil offers a more comparable basis and is generally used for the determination of the pH value.

EFFECT OF GRINDING OF SOIL ON THE HYDROGEN-ION CONCENTRATION

By grinding a soil to pass through a 100-mesh sieve Baver (*10*) found that the hydrogen-ion concentration of the acid samples of Wooster silt loam was not materially affected, but that with the alkaline samples the hydrogen-ion concentration was increased. This, it is stated, was probably due to the exposing of surfaces that had not been affected by the addition of lime. A decrease in acidity was found by grinding Brookston clay and Miami clay, glacial limestone soils. Dunkirk sand showed a large decrease in acidity after being ground. Sharp and Hoagland (*93*) observed, with the exception of one soil, that grinding a soil to pass a 200-mesh sieve did not materially alter the hydrogen-ion concentration of soil suspensions. Out of 5 acid soils, 2 showed no change and 3 showed a tendency toward a decrease in pH value, in one instance a decrease of 0.3 pH. With one alkaline soil, the exception previously mentioned, grinding increased the pH from 6.4 to 7.15.

For the determination of the hydrogen-ion exponents of soils it is preferable to use the unground sample.

SOIL-WATER RATIO

In the determination of the hydrogen-ion concentration of a soil the soil solution, suspension, and extract have been employed, the soil suspension and extract, however, being more generally used. The question naturally presents itself, What ratio of soil to water should be used?

Gillespie and Hurst (*49*) found an average positive difference for nine soils of 0.14 pH by varying the water-soil ratio from 1 to 1 to 2 to 1. This would indicate that at optimum moisture content the acidity may be more intense. In a subsequent publication (*50*) the same investigators found that the differences in exponents caused by varying the water-soil ratio from 1 to 1 to 2 to 1 are distributed like errors about a mean value of +0.04. There was no apparent correlation between the actual values of the exponent and the difference caused by dilution. Salter and Morgan (*92*) found that the pH value at a soil-water ratio of 1 to 5 varied from 0.10 to 0.85 pH higher than the calculated reaction at a field moisture content of 20 percent. They suggest a soil-water ratio of 1 to 5 as being suitable for colorimetric and electrometric procedures. For the acid soils investigated by these authors their electrometric results indicated a "systematic variation of hydrogen-ion concentration with variations in soil-water ratio, the highest hydrogen-ion concentration occurring

at high soil-water ratios, with a progressive decrease as dilution is increased."

Crowther (*36*) found a regular increase of about 0.1 pH for a two-fold dilution, varying the soil-water ratio from 1 to 1 to 1 to 32. Pierre's (*85*) work shows that when the soil-water ratio is varied from 1 to 2 to 1 to 50 the hydrogen-ion concentrations of some soils vary, whereas those of others show no differences. From the data it appears that the most acid soils studied are affected more by changing the soil-water ratio, and regardless of the soil texture this relation seems to hold. It is concluded by Pierre (*85*) that soils showing a change in hydrogen-ion concentration at different soil-water ratios do not show these differences after washing out the soluble salts and the more soluble acids. The acidity after washing is due entirely to the relatively insoluble acids. Further data given by Pierre show that the soil solution is not at a higher hydrogen-ion concentration than the 1 to 2 soil-to-water suspension or extract. From these data it is seen that the determination of the hydrogen-ion concentration of such soil suspensions or extracts is the same as that of the soil solution. Barnette, Hissink, and Van der Spek (*8*) concluded that the equilibrium with regard to the hydrogen-ion concentration between soil and water varies with the soil-water ratio and is dependent on many factors. The closer soil-water ratios (thicker suspensions) show a more constant hydrogen-ion concentration, and should, therefore, be used for the hydrogen electrode determination. Biilmann and Jensen (*20*) concluded that their results, in accordance with those of other investigators, show that the soil-water ratio is not without influence on the reaction of the soil-water mixture. The soil-water ratio seemed particularly important in acid soils (pH below 6.6 to 6.5), and, in all cases tested with lower pH values, the mixture becomes less acid upon dilution. Best (*14*) used a soil-water ratio of 1 to 5. The difference between the 1 to 1 and 1 to 5 ratios varied from 0.1 to 0.5 pH. For the majority of soils tested the difference was approximately 0.3 pH, the higher value being obtained with the more dilute suspensions. In a report (*94*) by the committee on soil reaction measurements of the International Society of Soil Science, it was stated: "The ratio of soil to liquid has not been examined by us and we therefore retain the 1 to 2.5 ratio adopted at the Gronigen Conference."

For most air-dried mineral soils the soil-water ratio of 1 to 2 is well adapted to the electrometric and colorimetric determinations of the hydrogen-ion concentration of soils. For peats or mucks the soil-water ratio may vary from about 1 to 3 to about 1 to 7.

DISTILLED WATER FOR USE IN PREPARATION OF SOIL SUSPENSION

In the preparation of soil suspensions or extracts the distilled water frequently receives little or no consideration as regards its pH value and specific conductance, both of which for ordinary once-distilled waters show considerable variation. The specific conductance of what may be termed nearly absolutely pure water, prepared by repeated distillation in vacuo is about 0.04×10^{-6} mho at 18° C. and when in equilibrium with atmospheric carbon dioxide is about 0.7 to 0.8×10^{-6} mho at 18° with a pH value of 5.7 (*1*). Only for special purposes, however, is water of such purity required. Acree and Fawcett (*1*) determined the pH changes caused by dilution of a

well-buffered medium such as Fermi's solution (containing 0.083 M phosphates) using double-distilled carbon dioxide-free pH 7.0 water (specific conductance about 0.3×10^{-6} mho at 18°), the same water air-equilibrated (pH 5.7) and ordinary distilled water from a commercial still and having the pH value 5.0. For dilutions greater than about 1 to 100, where the medium is very weakly buffered, differences in the pH value are produced by the use of pH 5.7 and especially 5.0 water as compared to the correct value obtained with pH 7.0 water and pH 7.0 indicator. For the preparation of soil suspensions Best (*14*) used air-equilibrated water of specific conductance 2 to 3×10^{-6} mho and pH value about 6. Biilmann and Jensen (*20*) determined the pH values of nine soils from about pH 4.7 to 8.2, using boiled distilled water free from carbon dioxide, aerated distilled water in equilibrium with the normal carbon dioxide pressure of the atmosphere, and ordinary distilled water without the carbon dioxide being removed. Their data show that the ordinary distilled water containing 17.2 mg of carbon dioxide per liter gave, with neutral and alkaline soils, results about 0.1 to 0.3 of a pH lower than obtained with the boiled distilled water or aerated distilled water, the aerated distilled water containing 1.0 mg of carbon dioxide per liter. The differences between the results obtained with the three types of water were small with the acid soils. Since the results with the boiled and aerated distilled water were in close agreement, Biilmann and Jensen recommend the use of either boiled or aerated distilled water.

In certain cases the use of so-called conductivity water may be necessary. However, for the determination of the pH value of soils, distilled water in equilibrium with atmospheric carbon dioxide and having a pH value of about 5.7 should be satisfactory, except in some instances, possibly, where the buffer capacity of a soil might be so low that the carbon dioxide content of air-equilibrated distilled water may be an interfering factor.

PREPARATION OF SOIL SAMPLE

The procedure for preparing the soil sample is similar to that described by the Association of Official Agricultural Chemists (*3*). The soil sample is air-dried in a room free from fumes and any soil lumps in the air-dried soil reduced by rubbing in a porcelain mortar or by any other equally effective method that will not reduce the rock fragments and the soil passed through a sieve having circular openings 2 mm in diameter. The sifted material is then thoroughly mixed.

ELECTROMETRIC METHODS

The methods for the determination of the pH value may be grouped under the two headings, electrometric and colorimetric. Under the electrometric method may be included the fundamental hydrogen-, the quinhydrone-, and the antimony-electrode procedures, and under the colorimetric method various adaptations of indicators to the determination of the hydrogen-ion exponent.

Other electrodes such as the glass electrode and different metal-metal oxide electrodes (*28, 33*) have been used for the determination of the concentration of hydrogen ions but their application to soils has up to the present been less extensive than that of the other electrometric methods. Recent work (*55, 81*) on soils using the glass electrode in the determination of the pH value and oxidation-

reduction potentials has shown good results. A review of the literature and the theory of the glass electrode have been given by Britton (*28*) and Clark (*33*).

The electrometric method consists essentially in the measurement of the potential difference between the soil as a hydrogen, quinhydrone, or antimony half cell and a standard half cell, such as a calomel half cell, the junction between the half cells being made with saturated potassium chloride solution. The potential difference is measured with some type of potentiometer in conjunction with a galvanometer or in some instruments the vacuum-tube principle is used. From the potential difference and observed temperature the pH is calculated by means of a working equation, or with some instruments the pH may be read directly.

DETAILS OF THE ELECTROMETRIC METHODS

ELECTROMETRIC SYSTEM

The electrometric system shown in figure 1 is mounted on a wooden base about 12 by 14 inches and placed upon a sheet of tin plate or copper for electrical shielding. The shaking apparatus is motor driven through pulleys *a* and *b* and connecting rod *d* which is connected to a crank pin on *b* and arm *e* which is connected to the crossbar *f*. The electrode vessels *n* swing through an angle of 45° (fig. 3) and within about 3° of the horizontal and are held by spring-clips attached to short rods connected to the crossbar *f*. Hydrogen is supplied to each vessel through rubber tubes connected to a copper tube *i* manifold the arms of which run under each vessel. The base of the manifold runs parallel to the crossbar *f* and is connected by means of a rubber tube to the glass tube and stopcock *j* to which is connected the hydrogen supply. The lead *l* from the saturated calomel half cell *c* and the lead *k*, are connected to the positive and negative terminals, respectively, of the potentiometer through a small switchboard or directly. It is advisable to have in the circuit a double-throw switch so wired that the polarity may be reversed if necessary, as in the case with the quinhydrone electrode when using a standard calomel half cell or in oxidation-reduction measurements.

For the measurement of the E.M.F (electromotive force) the writer uses a high-grade potentiometer and galvanometer in connection with a Bureau of Standards certified Weston cell (unsaturated type). The working cell for supplying current to the potentiometer is a 2-volt storage cell of about 65-ampere-hour capacity.

SHIELDING THE ELECTROMETRIC SYSTEM

Shielding against the effects of electrical leakage from high potential circuits is generally unnecessary where insulation is adequate, as is generally the case in dry weather. However, in damp weather, particularly, shielding is often very necessary. Where there exists a potential difference as a result of electrical leakage, for instance, from a 110-volt circuit, the measuring system may pick up this difference of potential. By the use of an equipotential shield the disturbing effects of electrical leaks may be eliminated. This may be accomplished by placing the potentiometer, cells, motor, etc., upon a sheet of metal such as tin plate or copper and if separate sheets are used

connecting each with a wire so that all parts of the shield are electrically in series. Insulated wires may be shielded by wrapping with tin foil and the tin foil soldered to a piece of wire with a drop of solder

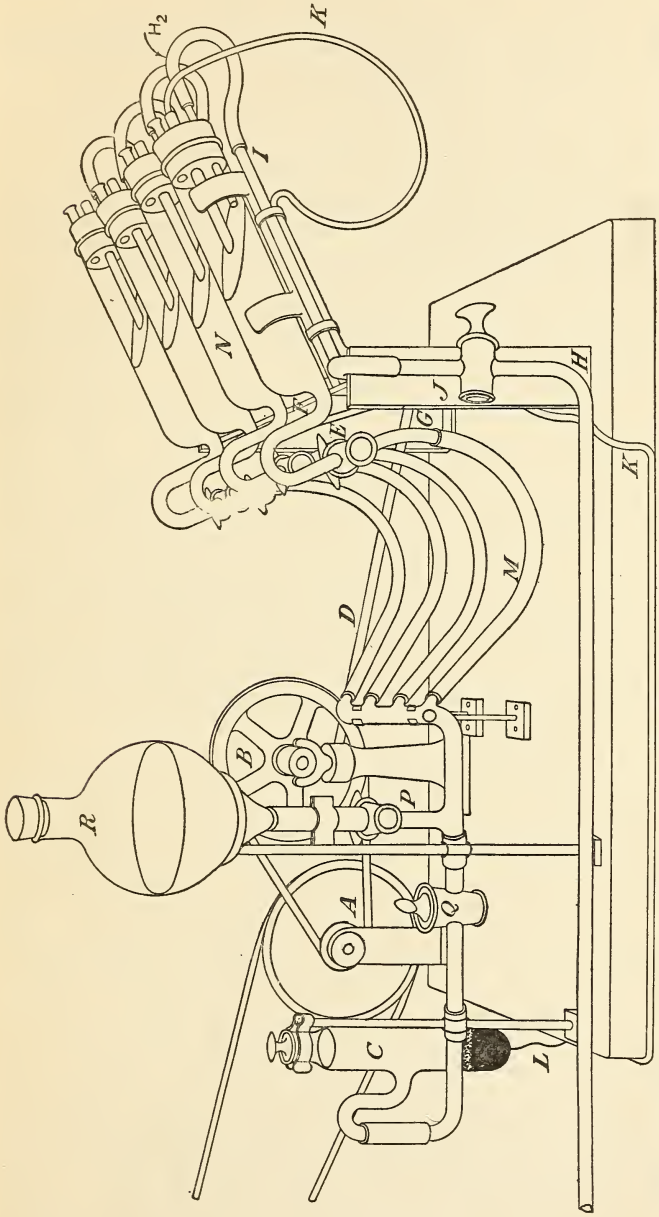

FIGURE 1.—Electrometric system: The rubber tubes *m* connect the electrode vessels with the glass manifold *o*, which is connected to the saturated potassium chloride reservoir *r* and the saturated calomel half cell *c* through stopcocks *p* and *q*, respectively. The 250-ml reservoir *r* and standard half cell *c* are held in place by metal supports which also support stopcocks *p* and *q*. Stopcock *q* is greased at the top and bottom leaving the middle ungreased. By greasing the large end of the key and the small end of the socket a conducting film of potassium chloride solution is obtained around the ungreased part of the stopcock when closed. Reservoir *r* is filled with saturated potassium chloride solution, and by means of stopcocks *p* and *q* the system is filled with potassium chloride solution. The ends of the rubber tubes *m* when not connected to the electrode vessels are closed with glass plugs. The filled side arm of the saturated calomel half cell *c* is connected to the rubber connection with care to avoid the entrance of air bubbles. Stopcock *q* is kept closed even during measurements. It is important in order to have good conductivity that the entire line be free from air bubbles.

and then connected to the remainder of the shield. The leakage current passes along the shield, and since the shield is a good conductor no appreciable potential difference is produced. The shield therefore

becomes an equipotential one, and any leakage voltage is reduced to a negligible fraction of a volt. The shield, preferably, should not be "earthed." Proper insulation, however, of the electrometric system is of prime importance. As stated by White (*106*):

> In general, the necessary and sufficient condition of this absolute protection is that the shield should interpose itself between the measuring system and the environment at every point where leakage can occur.

For further details regarding shielding the reader is referred to White (*106*).

CALOMEL AND OTHER STANDARD HALF CELLS

The calomel half cell, commonly referred to as a calomel electrode, generally consists of a layer of pure mercury covered with a layer of pure calomel containing finely divided mercury over which is a definite concentration of pure potassium chloride solution (0.1 N, N/1, or saturated) saturated with calomel. Contact with the potassium chloride solution may be made through a side arm, and contact with the mercury may be conveniently made by a platinum wire sealed in the base of the vessel (fig. 1, *l*). Contact with the mercury may also be made by a platinum wire sealed in the end of a mercury-filled center tube which passes through a rubber stopper in the top of the vessel. The 0.1 N and saturated calomel half cells are widely used, the 0.1 N being the better standardized and having a smaller temperature coefficient than the saturated calomel half cell. The saturated calomel half cell, however, is more extensively used as a working standard, in view of the fact that it does not necessitate the careful protection from concentration changes when using saturated potassium chloride solution for the elimination of liquid junction potentials as would be the case, for instance, with the 0.1 N or N/1 calomel half cells. Such protection of the standard half cell is very important. The calomel electrode vessel shown in figure 1, *c*, is about 2.5 cm in diameter at the base and 9.5 cm long, excluding the stopper, and has a volume of about 35 ml. Many variations in calomel-electrode design, each possessing its own features for its particular requirements, are described in the literature.

The preparation of the calomel half cell is as follows: To the thoroughly clean and dried vessel is added especially pure mercury (*33*) sufficient to cover the platinum wire and prevent its coming in contact with the solution in event of accidental jarring. Over the mercury is placed a layer of pure calomel (0.5 to 1.0 cm deep) preferably the electrolytic calomel which contains very finely divided mercury. The electrolytic calomel may be prepared as described by Clark (*33*) or purchased. If chemically prepared calomel is used it is better to shake this with mercury rather than grind it, in order to avoid a variation in the grain size of the calomel which may affect the potential. The calomel, before being added to the vessel, is shaken with several changes of the especially pure potassium chloride solution to be used in the half cell, each time allowing the calomel to settle and then pouring off the supernatant liquid. After adding the calomel to the half cell the vessel is carefully filled with the potassium chloride solution to be used, which has been saturated with calomel. For this purpose a reserve supply of the potassium chloride solution is made up and saturated with calomel. After preparing the saturated calomel half cell, some crystals of potassium chloride are added.

Another type of standard half cell described by Veibel (*103*) is a quinhydrone electrode in which a solution of known pH value is used. The stock solution, namely, 0.09 N KCl and 0.01 N HCl, the pH value of which is 2.03 is prepared by mixing 900 ml of 0.10 N potassium chloride and 100 ml of 0.10 N hydrochloric acid (*20*). The standard half cell is prepared by shaking about 25 ml of this solution with about 0.1 g of quinhydrone and adding to the electrode vessel such as in figure 1, *c* (without platinum wire *l*,) after which a bare platinum foil electrode, inserted in a rubber stopper, is placed in the vessel. According to Veibel (*103*) the reproducibility of this half cell is equal to that of the calomel half cell and the durability is satisfactory for the first 48 hours. However, Biilmann and Jensen (*20*) recommend preparing the half cell fresh daily.

Since there is no adequate method for measuring the potential of a single electrode, an arbitrary standard, the normal hydrogen half cell, has been adopted, and its potential called zero. The normal hydrogen electrode is a hydrogen electrode under one atmosphere pressure of hydrogen in a solution of unit hydrion activity, the potential being considered zero at all temperatures. The potential of a whole cell is therefore assigned to the half cell joined to the standard which is zero potential. Instead of preparing a normal hydrogen half cell each time and standardizing it by an independent method, it is more convenient to use a working standard such as a calomel half cell the value of which has been determined by comparison with a normal hydrogen half cell. The observed potential between a hydrogen and a calomel half cell may be corrected by the value for the calomel half cell and then the corrected potential can be considered as the potential between the unknown hydrogen half cell and the standard. The calomel half-cell values given by Clark are shown in table 2. The italic figures in table 2 were used as reference values for calculating the remaining values by means of the temperature coefficients.

TABLE 2.—*Calomel half-cell values*

[Referred to normal hydrogen electrode]

Temperature	KCl concentration		Temperature	KCl concentration	
°C.	0.1 N	Saturated	°C.	0.1 N	Saturated
	Volts	*Volts*		*Volts*	*Volts*
18	*0.3380*	0.251	35	0.3365	0.238
20	.3379	.250	38	.3361	.236
25	.3376	*.2458*	40	.3358	.234
30	.3371	.242			

JUNCTION BETWEEN HALF CELLS

The junction between half cells, such as the hydrogen, quinhydrone antimony, etc., and a standard half cell has been made in a variety of ways, such as with membranes, flowing junctions, a mixture of agar-agar and potassium chloride, a saturated solution of potassium chloride; etc. However, liquid contact is preferable.

Since contact of two solutions of different composition produces a potential difference at the plane of contact, it is important that this diffusion potential be greatly reduced or eliminated if possible. The cause of the diffusion potential may be attributed to unequal ionic

mobilities. It has been found that the interposition of a saturated solution of potassium chloride, the ions of which have approximately the same velocity, will in most cases (excepting very acid and very alkaline solutions) practically eliminate the diffusion potential so that there is maintained a constant and very small liquid junction potential. In some instances the junction between the standard half cell and the soil as a hydrogen or quinhydrone half cell has been made by means of a capillary tube containing a saturated solution of potassium chloride in direct contact with the soil suspension, but it is well to avoid the formation of liquid junctions within capillaries and also the diffusion of potassium chloride into the soil suspension. With the electrode vessel used by the writer (fig. 3), contact of the soil suspension with the saturated potassium chloride solution is made outside of the vessel proper, and any danger of contamination of the soil suspension with potassium chloride is eliminated.

The agar bridge is frequently used (*20, 31*) for making junctions and may be prepared by heating 5 g of agar-agar with 100 ml of saturated potassium chloride solution to almost boiling until the agar-agar has dissolved, replacing any water lost by evaporation. The mixture is allowed to cool until nearly solidified and then drawn into a clean, dry, U tube of about 4 mm internal diameter which is left in the agar-agar until the mixture has solidified. The tube, which must be entirely filled with the agar mixture adhering firmly to the tube, is trimmed off even at the ends. The ends of the tubes may be left in saturated potassium chloride solution to prevent drying of the agar-agar and diffusion of the salt. The ends of the tubes before use should be washed with distilled water and the end in the soil kept in contact with the soil suspension only during the potential measurement. The junction between the half cells is made by dipping one end of the agar tube into the soil suspension and the other end into a small intermediary vessel containing saturated potassium chloride solution into which also dips a side arm contact from the standard half cell. The intermediary vessel is closed with a rubber stopper having holes for the agar tube and side-arm of the half cell. With the arrangement shown in figure 1, saturated potassium chloride solution is used for the external liquid junction; however, this same arrangement has been used with the agar bridge and the bubbling hydrogen electrode. One end of the agar bridge is dipped into the soil suspension and the other end connected to the potassium chloride filled rubber tube (fig. 1 *m*) which has been swept free of any air bubbles by opening stopcock *p*. The standard half cell is protected by the closed, "half-greased" stopcock *q*.

Some objection has been raised to the use of the agar-potassium chloride bridge dipping directly into the suspension, due to the diffusion of potassium chloride into the soil suspension. In this connection it is stated by Best (*14*) that in all cases lower pH values were obtained with a bubbling hydrogen electrode (fig. 2, *D*) using an agar KCl junction dipping directly into the suspension than with another type of vessel (Crowther vessel, fig. 2, *C*) having an external liquid junction. Tests showed that these lower values were due largely to the action of potassium chloride although the agar bridge was placed in the suspension only just prior to a measurement. It was concluded by Best that this type of vessel (fig. 2, *D*) using the agar-potassium chloride bridge may be used without any great

error with certain soils, but many Australian soils appear to be too susceptible to traces of potassium chloride to permit its use. With three alkaline soils the values obtained with this vessel although steady and reproducible were lower than obtained with the Crowther vessel (using an external liquid junction) by 0.17, 0.22, and 0.24 pH. Hissink and Van der Spek (*59*) determined the amount of potassium chloride passing from an agar bridge (glass capillary) into 20 ml of distilled water, the quantity of water used by them for 5 g of soil with the quinhydrone electrode. After 3 and 22 hours, respectively, the liquid was 0.0002 N and 0.0005 N in respect to potassium chloride. Biilmann and Jensen (*20*) determined the effect of potassium chloride on the pH values of five different soils using a soil-water ratio of 1: 2. The pH values of the soils in 0.0001 M potassium chloride were practically identical with those obtained in aqueous suspension. In 0.001 M potassium chloride the decreases in pH ranged from 0.07 to 0.17. With increasing concentration of potassium chloride the decrease in pH was greater. Biilmann and Jensen (*20*) concluded that since a measurement as a rule requires only a few minutes there should be no error caused by salt diffusion from the agar tube. Biilmann and Jensen (*20*) further state that the small amounts of potassium chloride are transferred to the soil suspension not so much by diffusion as by siphonage through the tubes and agar mass and that the siphonage may be prevented by keeping the surface of the soil suspension higher than the surface in the intermediary vessel contacting the standard half cell. With the quinhydrone electrode the agar tube is inserted in the upper region of the suspension only at the time of measurement which is made after the suspension has been shaken, i.e., with the suspension at rest. Under these conditions the effect of any diffused potassium chloride on the pH value of the suspension may be reduced to a minimum. For most well-buffered soils the effect of the agar bridge on the pH value may not be significant; however, this may not be the case for poorly buffered soils or extracts, particularly when the soil suspension is agitated during the measurement as with the hydrogen electrode, in which case any diffused potassium chloride would be distributed throughout the suspension. By the use of an external liquid junction (fig. 3) any danger of potassium chloride diffusing into the suspension is eliminated.

CHECKING THE ELECTROMETRIC SYSTEM

In the electrometric determination of hydrogen-ion concentrations it is essential that the electrometric system be frequently checked. To frequently check the entire electrometric system in detail would be quite troublesome; however, this may be conveniently done by making a measurement upon a buffer solution, the value of which has been accurately determined. If the observed potential of the cell is in agreement with the accepted value it is reasonably safe to assume the accuracy of the system throughout. While there are numerous buffer solutions which may be used for this purpose the M/20 acid potassium phthalate standard of Clark and Lubs (*33*) has been widely used and is easy to prepare.

A stock solution is prepared as M/5 containing 40.836 g of acid potassium phthalate in 1 l of the solution and 50 ml of this solution diluted to 200 ml to give the M/20 solution for use as the standard buf-

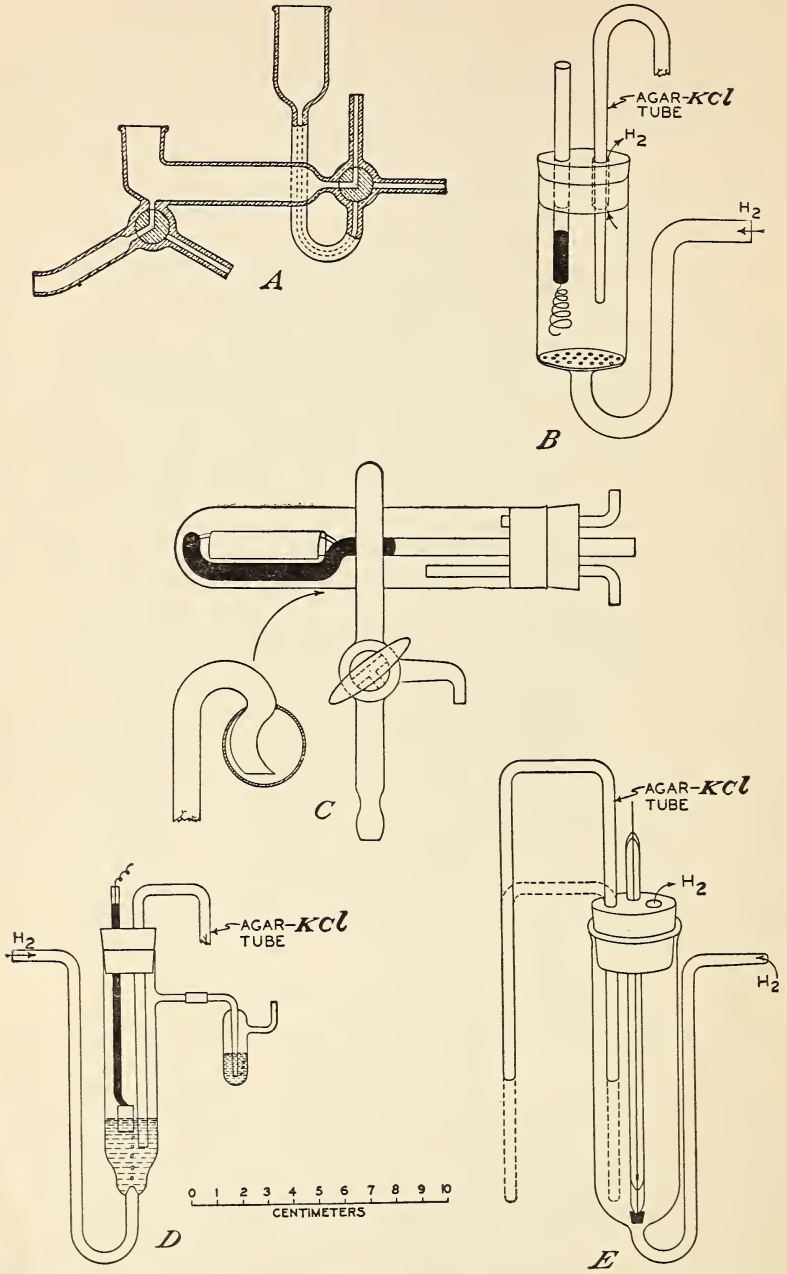

FIGURE 2.—Hydrogen electrode vessels of Clark (*A*), Bray (*B*), Crowther (*C*), Best (*D*), and Bailey (*E*) types.

fer. The value 40.836 g used by Clark and Lubs when the solution was standardized should be used for preparing the M/5 solution. Clark suggests the use of redistilled water for the preparation of the stock solution. The M/20 acid potassium phthalate standard has the pH value 3.974 at 20° C. (*33*).

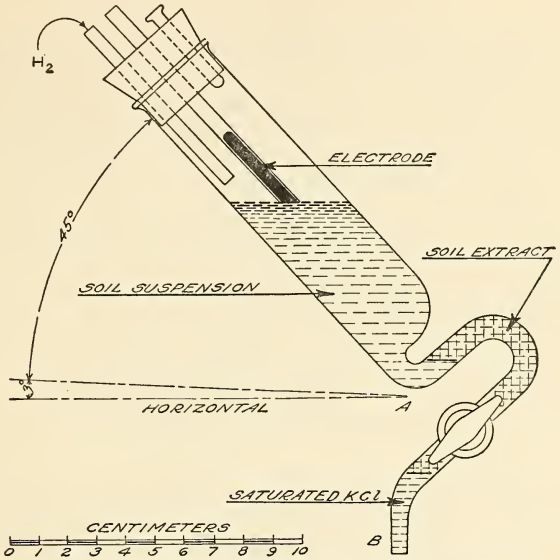

FIGURE 3.—The filled electrode vessel; *A*, axis; *B*, end tube.

The following tentative values are given by Clark (*33*) (table 3) on the assumption of inappreciable alteration in the pH value of M/20 acid potassium phthalate between 18° and 40° C.

TABLE 3.—*Values for acid potassium phthalate standard* [1]

t °C.	Half cell 1	Cell 2	Cell 3	*t* °C.	Half cell 1	Cell 2	Cell 3
	Volts	*Volts*	*Volts* [2]		*Volts*	*Volts*	*Volts* [2]
18	−0.2292	0.5672	0.480	35	−0.2426	0.5791	0.481
20	−.2310	.5689	.481	38	−.2449	.5810	.481
25	−.2347	.5723	.481	40	−.2465	.5823	.481
30	−.2386	.5757	.481				

[1] Half cell 1: Pt, H_2 (1 atmosphere) | KHPhthalate 0.05 M | KCl (saturated) ‖ Cell 2: half cell 1 | KCl (saturated) | KCl (0.1N), HgCl | Hg Cell 3: half cell 1 | KCl (saturated), HgCl | Hg.

[2] Approximate.

HYDROGEN ELECTRODE METHOD

The hydrogen electrode method for determining the pH value of soils consists essentially in the measurement of the E.M.F. of a cell, composed of a hydrogen half cell (the soil) and a standard half cell, from which observed E.M.F. and temperature the pH value is calculated.

HYDROGEN HALF CELLS

The hydrogen half cell is composed of a noble metal, such as platinum or gold coated with palladium, platinum, or iridium black, placed in a solution of hydrogen ions under a definite partial pressure of hydrogen.

HYDROGEN-ELECTRODE VESSELS

Many designs of electrode vessels used in the determination of the hydrogen-ion concentration of soils will be found in the literature and also described by Clark (*33*). By shaking the hydrogen electrode vessel Hasselbalch (*52*) was able to obtain constant potentials in a short time. The application to soils of the principle of shaking the vessel, together with alternate immersion of the electrode in the suspension (*37*, *38*) and exposure to the hydrogen of the electrode carrying a film of solution allows a speedy attainment of equilibrium between the gaseous hydrogen, the electrode, and the soil suspension. Under these conditions a localized equilbrium is avoided and one more characteristic of the entire suspension obtained. Shaking mechanically or by hand, bubbling hydrogen through the suspension, or mechanical stirrers have been employed for keeping the soil in suspension. Two types of hydrogen-electrode vessels quite generally used for soils are the closed type and the bubbling hydrogen type.

The closed type of electrode vessel of Pyrex glass used by the writer for soils is shown in figure 3. It is a modification of the one designed by Gillespie (*46*) and has a volume of about 70 ml. The bore of the stopcock is 3 mm. The essential features recommended by Clark (*33*) are embodied in the vessel. The hydrogen electrode is alternately exposed to the hydrogen and submerged in the suspension, the potassium chloride liquid junction with the standard half cell is made outside of the vessel proper and the hydrogen is not bubbled through the suspension. During mechanical shaking the hydrogen electrode is never entirely out of contact with the soil suspension. A widely used closed type of electrode vessel is that designed by Clark (*32*, *33*) (fig. 2, *A*). It is intended for liquids but was used by Healy and Karraker (*54*) for soils. Knight's vessel (*65*) is a tube closed at both ends with an opening near each end for the electrode and hydrogen and for the contact with the standard half cell. Crowther's vessel (*36*) (fig. 2, *C*) designed for soils is a modification of Clark's vessel and embodies the principles of alternate exposure and immersion of the electrode and making liquid junction with the standard half cell outside of the vessel. Best in a comparative study of methods (*14*) concluded that no one method for determining the pH value of soils can be regarded as universally applicable, but that the Crowther modification (*36*) of the Clark hydrogen-electrode vessel approaches this ideal very closely. A hydrogen-electrode vessel with external liquid junction developed by Bollen (*25*) makes use of a centrifugal circulator or stirrer which circulates a small constant volume of hydrogen under constant pressure through the liquid. It is especially applicable to solutions or suspensions of alkali soils containing carbonates. Compared with a bubbling hydrogen electrode, the two electrodes agreed only on solutions free from carbon dioxide. The greater the carbon dioxide content the greater the difference in results due to the

removal of carbon dioxide by the bubbling electrode with a subsequent shift in the acid-base equilibria and rise in pH.

A bubbling-type hydrogen-electrode vessel described by Pierre (*85*) is one in which the soil is kept in suspension by hydrogen bubbling up through the bottom of the vessel. The junction between the standard half cell and the soil suspension is made by an agar-potassium chloride bridge. Bray's vessel (*26*) (fig. 2, *B*) consists of a Gooch funnel (with the stem bent up) in the bottom of which is sealed a perforated porcelain plate through which hydrogen is bubbled rapidly enough to give the soil suspension the appearance of boiling. Best (*12*) designed a bubbling hydrogen-electrode vessel (fig. 2, *D*) similar in principle to Bray's and Heintze and Crowther's sintered-glass crucible vessel (*56*) and used it with excellent results with other solutions, but when tried on soil suspensions it gave low values in all cases as compared with Crowther's vessel (*36*). Best's objections to its use for soils were that the potassium chloride diffusing from the agar bridge, dipping directly into the suspension, is dispersed by the action of the bubbling hydrogen and the fact that the bubbling hydrogen may affect the carbonate equilibria. Bailey's (*6*) bubbling hydrogen electrode (fig. 2, *E*) is similar to those described by Pierre (*85*), Bray (*26*), and Best (*12*). Hildebrand's bubbling electrode vessel (*58*) is a tube, one end of which is immersed in the solution permitting the hydrogen escaping from the end of the tube to alternately expose a central electrode to hydrogen and bathe it with the solution. In a report (*94*) of the committee on soil reaction measurements of the International Society of Soil Science a sintered-glass crucible or funnel is recommended as a convenient bubbling hydrogen-electrode vessel. The sintered-glass filter should be sufficiently coarse-grained to permit a rapid flow of hydrogen. When using the crucible a rubber stopper holding a tube for supplying hydrogen is inserted below the sintered-glass plate. It is also stated that with alkaline soils, especially in the naturally moist state, the removal of carbon dioxide by the current of hydrogen introduces an error and it is better to use a closed vessel of the Clark type (fig. 2, *A*).

HYDROGEN ELECTRODE BASE

A piece of platinum wire, foil, or gauze will serve as the base of the hydrogen electrode. The platinum wire and foil are preferable, as the gauze presents cleansing difficulties. If foil is used it may be welded to a short piece of platinum wire, the wire sealed into a glass tube, and mercury poured in for electrical contact. The welding may be accomplished by placing the foil and wire in contact on a piece of polished steel and striking with the polished end of a small hammer while heating to white heat with a blast lamp. For convenience in welding the electrode the writer designed the apparatus shown in figure 4. It is made of steel with a base about 7.5 cm in diameter and a supported plunger about 6 mm in diameter held in place about 2 cm above the base by a spring. The platinum to be welded is placed in the proper position directly under the plunger, then heated to white heat with a blast lamp, and the plunger struck with the hand. By this means the direction of the blow is controlled and the electrode is not scarred. The glass tubing to which the electrode base is sealed should have a coefficient of expansion similar

to that of the platinum. Since the design and size of the electrode permit of many types, mention will be made of only a few. Gillespie's electrode (fig. 5 *A*) as used by the writer was made from a rectangular piece of platinum foil 2.5 by 3.0 cm, although 1 inch square is satisfactory. Short lengths of platinum wire are welded to the middle of each end of the foil and serve as leads for the current and supports for the electrode. The foil is then rolled by means of a glass tube into a U shape so that the sides are about 1 cm apart. The platinum leads are inserted through openings in the soft glass support and then sealed and the glass annealed. Electrical contact is made by pouring mercury into the electrode. An electrode similar to figure 5 *B*, but 1 inch square, has also been used in place of the rolled electrode; however, an electrode of that size and with only a single support is inclined to bend too easily. The platinum foil was 0.005 inch thick and the wire 0.015 inch in diameter. Clark (*33*) recommends a piece of foil about 1 centimeter square, 0.08 mm thick, welded to a wire 0.08 mm in diameter. A soft glass tube is drawn down and the capillary end broken off close to the shoulder of the tube. The platinum wire is inserted until the foil is in contact with the glass, and then with the tip of a flame a perfect seal is made and a little of the glass sealed to the foil, so that the foil

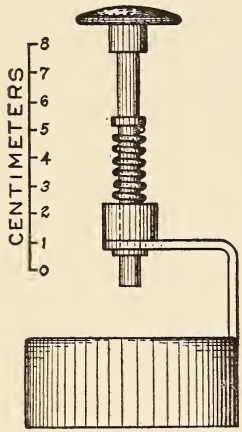

FIGURE 4.—Electrode welding hammer.

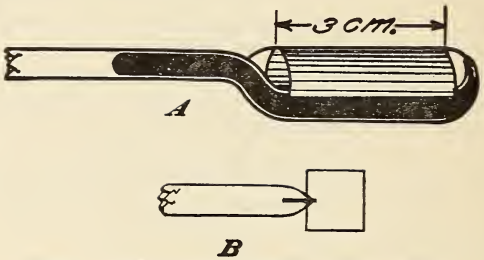

FIGURE 5.—Electrodes of Gillespie (*A*) and another (*B*) type.

slightly recesses in the glass. This type of electrode (fig. 5 *B*) is quite widely used. Clark (*33*) calls attention to the fact that the most frequent mistake in making electrodes is the use of too large a wire. Sharp and Hoagland (*93*) used a Cottrell hydrogen electrode consisting of a glass tube about 15 cm long and 1 cm in diameter, in one end of which is sealed a cylinder of fine platinum gauze about 1 cm long and near the other end of which a side tube permits the entrance of hydrogen. Knight's electrode (*65*) is a rectangular piece of platinum 1.2 by 2.4 cm, with platinum wires welded to each end for sealing to a glass tube.

In regard to sealing platinum leads into the glass support some investigators have reported considerable difficulty due to the creepage of mercury through a crack in the glass at the point of seal. After sealing the platinum lead into the glass the seal should be carefully annealed and allowed to cool and then closely examined for any cracks.

Morgan, Lammert, and Campbell (*79*) recommend that, from the point of view of the reproducibility of different pieces of the same

metal when used for the quinhydrone electrode in 0.1 N HCl in the presence of air, pieces of platinum foil, preferably old and roughened, of at least 1 cm^2 surface be sealed into soft glass tubing and carefully annealed; and in addition that electrodes so made be tested for leaks by boiling in hot water.

CLEANING OF ELECTRODE

It hardly seems necessary to mention that a high degree of cleanliness of the electrode is essential. The electrodes are frequently cleansed by carefully heating in chromic-sulphuric acid cleansing solution and then allowing to cool. When not in use they are kept in this solution. In regard to cleaning electrodes for use as a quinhydrone electrode in 0.1N hydrochloric acid, Morgan, Lammert, and Campbell (*79*) state that the electrodes after being filled with mercury should be immersed in cold chromic acid cleaning mixture prepared from chemically pure chemicals, then heated to about 125° C. and slowly cooled, the electrodes being short circuited in pairs. The electrodes are then carefully rinsed in distilled water and in alcohol and dried for about 20 minutes in a current of purified air and then used. Occasionally, the customary cleaning procedures may not be adequate thoroughly to clean the electrodes, so recourse may be had to a very fine polishing agent such as crocus cloth or very fine emery powder. A test of the cleanliness of an electrode is the evenness with which the bubbles of hydrogen escape from the entire surface of the electrode when electrolyzed in dilute sulphuric acid (10 percent). Cleanliness of electrodes is particularly stressed by Biilmann (*19*) for the quinhydrone electrode, in which case he recommends, in addition to cleaning solution, heating of the electrodes to redness in the alcohol flame but not in the ordinary gas flame. The disadvantage, however, is the danger of cracking the glass. Morgan, Lammert, and Campbell (*79*) concluded that the results obtained when the electrodes are heated in an alcohol flame before use do not justify the method in view of the large number of electrodes which crack.

COATING OF ELECTRODE

For coating electrodes, solutions of palladium chloride ($PdCl_2$), iridium chloride, and chloroplatinic acid have been used. (*2*, *33*). Three-percent solutions acidified with hydrochloric acid are generally used. A current of about 0.8 ampere at 4 volts was used for coating and subsequent treatment of the electrodes and was taken from a 220-volt lighting circuit by using the proper resistance, or a 4-volt storage battery or dry cells may be used. Connections are made to three small platinum electrodes in three small vessels, the positive terminal being connected to two of the electrodes and the negative terminal to the other. Palladium is quite extensively used for coating the electrodes as it is easily removed from the platinum electrode by electrolysis in dilute hydrochloric acid. For coating the electrodes with palladium an approximately 3-percent solution of palladium chloride containing about 2 percent of concentrated hydrochloric acid by volume is used, the concentration of palladium being maintained by the occasional addition of 5-percent palladium chloride solution. This solution is added to one of the vessels with a positive electrode while to the other vessel with a positive electrode is added 10 percent sulphuric acid and

to the remaining vessel with the negative electrode is added 1+1 hydrochloric acid. Before coating the electrode it should be particularly clean and well washed with distilled water. A negative lead is connected to the electrode, which is then lightly coated in the palladium chloride solution in about 5 seconds. It is then thoroughly washed under a vigorous stream of distilled water and the negative lead again connected to the electrode which is electrolyzed for about 10 seconds in the 10-percent sulphuric acid so as to charge it with hydrogen. It is again thoroughly washed in distilled water and then used. The previous coating may be removed by connecting the positive lead to the electrode and electrolyzing in the 1+1 hydrochloric acid.

In regard to the thickness of the coating some prefer a fairly light coat while others prefer a heavy one. With too heavy a deposit of "black" there exists the possibility of occlusion, particularly of acid, during the preparation of the electrode. The "black" should be evenly deposited and the presence of any bright spots should be sufficient reason for cleaning and recoating the electrode. Sometimes when removing the wire lead from the electrode after plating, a few drops of mercury may accidentally spill on the electrode and amalgamate with the palladium, in which case the electrode should be cleaned by electrolysis in 1+1 hydrochloric acid and then recoated.

DIFFICULTIES IN HYDROGEN-ELECTRODE MEASUREMENTS

In the electrometric determination of hydrogen-ion concentrations difficulties often arise, the causes of which frequently require considerable time to locate. A few such disturbances which may prove quite disconcerting are cited. In damp weather especially, electrical leakage and improper shielding of the electrometric system may account for considerable annoyance. Occasionally erratic potentials or poor conductivity may be traced to an air bubble in the saturated potassium chloride line or with the hydrogen electrode to a bubble of gas in the bore of a stopcock on the electrode vessel. Unclean electrodes, poor coating of "black", impure hydrogen, or an insufficient supply of pure hydrogen are often sources of trouble. Occasionally an electrode may develop a small crack where the platinum is sealed into the glass, thus permitting the creepage of mercury through the crack.

In the presence of oxidants, such as nitrates, dissolved oxygen, ferric iron, etc., the hydrogen electrode as a rule cannot be used. With soils the concentration of such reducible substances is generally low and the hydrogen electrode may therefore be considered applicable for the majority of soils. As stated by Clark (*33*):

> It is impracticable to list all the systems which are incompatible with a hydrogen electrode potential. The practical way to deal with the problem is to assume that a rapid attainment of electrode equilibrium and its maintenance after attainment is evidence that the small amounts of oxidants, such as oxygen, ferric iron, etc., which are frequently present, have been reduced and that no important consituent of the solution is "depolarizing" the electrode.

Regarding the effects of nitrates, Joseph and Martin (*62*) found that a neutral 1-percent solution of sodium nitrate through which hydrogen was slowly passed for 5 hours in the presence of a few square centimeters of platinized platinum foil, reached a pH of more than 10 and gave a heavy precipitate with Nessler's reagent. Results on one soil of pH 9.42 and containing no nitrate showed that adding 200 p.p.m. of $NaNO_3$ changed the pH value to 9.41; 500 p.p.m. to 9.34 and 2,000

p.p.m. to 9.10. These authors state that only when the amount of nitrate in the soil reaches a figure quite beyond that for a normal soil does the disturbing effect manifest itself, and concluded that no disturbing effect is likely to be introduced by nitrates up to 500 p.p.m. of soil. Sharp and Hoagland (*93*) state that while with extracts of acid soils the reduction of nitrates precludes the use of the hydrogen electrode it is not believed that appreciable errors would be caused in the case of nutrient solutions containing nitrates. Gillespie and Hurst (*50*) observed that the hydrogen-ion concentration of the extract comparatively free from soil particles was indefinite and meaningless, this being attributed to the presence of nitrates in a solution weak in buffer action.

Under the heading of poisons, are listed a number of substances which affect the catalytic activity of the coating of black on the hydrogen electrode thus causing the electrode to function improperly. The electrode is then said to be "poisoned." A number of such poisons are discussed by Clark (*33*) and Britton (*28*) among which may be mentioned the deposit of films of protein and of colloidal material, As_2O_3, $HgCl_2$, etc. Clark (*33*) states with reference to free ammonia and hydrogen sulphide, that there is no special difficulty in obtaining hydrogen-electrode potentials agreeing with colorimetric measurements in bacterial cultures containing distinct traces of ammonia or hydrogen sulphide.

In regard to $HgCl_2$, a soil sample submitted to the writer gave with a hydrogen electrode a negative potential and a correspondingly absurd pH value for a soil. It was noticed that the box in which the soil had been sent was labeled "Bichloride of Mercury." The treatment of 15 g of a similar sandy soil low in organic matter with as little as 10 mg of $HgCl_2$ produced an effect greater than that mentioned above. This apparently was an instance of "electrode poisoning." The effect on other soils higher in organic matter was comparatively small. A second sample of the original soil, but free from $HgCl_2$, was found to have a pH value of 5.3.

For further details in regard to difficulties with and limitations of the hydrogen electrode the reader is referred to Clark (*33*) and Britton (*28*).

HYDROGEN-ELECTRODE PROCEDURE

The hydrogen-electrode procedure for the determination of the pH value of soils using the closed type of hydrogen-electrode vessel (fig. 3) is as follows: 15 g of air-dried soil (passing a 2-mm sieve) and 30 ml of distilled water are shaken in a large rubber-stoppered Pyrex test tube for approximately 1 minute. If desired, sufficient samples may be prepared for half a day's work. The suspension is allowed to stand about 20 minutes or longer for sedimentation and to approach equilibrium, and enough of the supernatant liquid to fill the neck of the vessel and bore of the stopcock is poured into the electrode vessel (fig. 3) and the stopcock closed. The end-tube *B* is then filled with saturated potassium chloride solution and the vessel attached to the shaker (fig. 1). Contact with the saturated calomel half cell is made through the rubber tubing (fig. 1, *m*), which is swept free of air bubbles by means of saturated potassium chloride solution from reservoir *R* and then connected to the electrode vessel, the entrance of air bubbles being avoided. The remainder of the soil suspension is shaken up and poured into the vessel. The elec-

trode (fig. 5, *A*) is coated with palladium for each determination and inserted into a rubber stopper containing an inlet and outlet for the hydrogen (fig. 3). The electrode is then washed and placed in the vessel convex side up (fig. 3) and about 1 cm from the bottom, so that when the vessel rocks to its lowest position only the edges of the electrode are in contact with the suspension and the convex side exposed to the hydrogen. The hydrogen supply is attached to the vessels as shown in figure 1, the outlet plugs in the rubber stoppers temporarily removed, stopcock *j* opened (and left open during the determination) and the atmosphere above the suspension thoroughly swept out with pure hydrogen, but not bubbled through the suspension, and then the outlets are closed. If desired the first vessel may be swept out with hydrogen while the second is being filled with the suspension and so on for the remaining vessels. A glass T-tube, safety valve, one end of which dips under mercury, is inserted between the hydrogen tank and stopcock *j*. The hydrogen supply is closed at the tank and an outlet plug on one of the vessels removed for a second to relieve any excess pressure in the line. The negative lead from the potentiometer is inserted into the first electrode and the vessels shaken at the rate of 70 to 85 complete swings per minute. After 5 minutes, and without interrupting the shaking, the liquid junction is drawn into the end-tube *B* (fig. 3) of the first vessel, the potential measured and the stopcock on the vessel closed. Shaking is momentarily stopped to transfer the negative lead successively to the remaining vessels, and the measurements are made during shaking. After 5 minutes additional shaking the measurements are repeated, as a check on the constancy of potential. All potentials are measured during shaking. The liquid junction is drawn into the end-tube *B* of the electrode vessel during shaking, by opening stopcock (fig. 1, *p*), pinching the connecting tubing *m*, closing stopcock *p*, and then opening the stopcock on the electrode vessel and gradually releasing the pinch, thus preventing the entrance of potassium chloride into the suspension. Equilibrium is obtained in about 5 minutes and the reproducibility of the determinations is generally within 3 millivolts (*96*). After the determination the tubing (fig. 1, *m*) is flushed out with potassium chloride solution and closed with a glass plug.

It has been observed that if the electrode vessel is not shaken during the measurement the potential sometimes increases so rapidly that any measurement would be a forced one, and readings made after the potential seemed to become constant would in general appear to be in error. From the observed potential difference and temperature the pH value is calculated. The temperature was read from a thermometer in a test tube of water mounted on the base of the shaking apparatus. All measurements were made with a high-grade potentiometer and galvanometer in connection with a Bureau of Standards certified Weston cell (unsaturated type).

A somewhat simplified hydrogen-electrode procedure which is quite widely used is one in which a bubbling hydrogen electrode vessel is employed, several types of which (Bray, Best, and Bailey) are shown in figure 2. The procedure is as follows: A series of soil suspensions may be prepared as previously described for the closed type hydrogen electrode vessel. Bailey (*6*) used with his vessel (fig. 2, *E*) when possible, 1 part of soil by volume and 2 parts of

distilled water, preparing enough samples for half a day's work. A spoon holding 1½ ml of soil when level full was used as a measure and to this quantity was added 3 ml of boiled distilled water and the whole shaken in a rubber-stoppered Pyrex test tube. For clays, twice that amount of water is used. Bailey (*6*) states that it appears to make no difference whether the water stands on the soil for 5 minutes or for 6 or 7 hours. While the hydrogen is flowing through the vessel the soil suspension is shaken up and transferred to the vessel. The hydrogen bubbles through the suspension during the entire determination, the flow being regulated so as to keep the soil in complete suspension and give the appearance of boiling. With Bailey's vessel (fig. 2, *E*) a 3-holed rubber stopper carrying a palladium-coated electrode is inserted into the vessel so that the coated electrode is completely submerged in the suspension. Bailey states (*6*) that with acid soils equilibrium is obtained in from one-half to 5 minutes, whereas alkaline soils require from 5 to 10 minutes. Just before measuring the E.M.F. the washed agar tube is inserted through one of the holes in the rubber stopper until it makes contact with the suspension. The E.M.F. is read while the hydrogen is bubbling through the suspension. The writer was advised by Bailey that duplicate determinations using his hydrogen-electrode vessel generally agree within 0.05 pH.

With the sintered-glass crucible or funnel recommended by the committee on soil reaction measurements of the International Society of Soil Science (*94*) it is stated that the platinum or palladium coating on the electrode should be very thin, only a few millimeters of the electrode are immersed in the soil suspension and the agar-potassium chloride bridge should not be lowered into the suspension until immediately before the potential measurement. Under these conditions it is claimed that constant potentials may be obtained within about 1 minute.

In the determination of hydrogen-ion concentrations it is of foremost importance that the reliability of the measurement be established. In regard to the hydrogen electrode the E.M.F. should be reproducible with different vessels and different electrodes and in addition it should be stable. When using flowing hydrogen (*33*) the potential should be the same with different rates of flow. It should be remembered, however, that the hydrogen electrode is not universally applicable, particularly in the presence of unsaturated organic compounds and active oxidizing agents, and there may be soils containing constituents which would cause unsatisfactory results and preclude the use of the hydrogen electrode. If such instances should present themselves in the case of soils, if there is reason to suspect the validity of the results, or if difficulty is had in obtaining stable and reproducible potentials with the hydrogen electrode, it is advisable to compare the results with those by other methods. It has been the writer's experience with many thousands of soil samples that instances when the hydrogen electrode (fig. 3) cannot be used are few.

HYDROGEN-ELECTRODE EQUATIONS FOR CALCULATING pH VALUE

The hydrogen-electrode equation for calculating the pH value, (partial pressure of hydrogen one atmosphere) using a standard calomel half cell is as follows:

$$(1) \qquad \mathrm{pH}=\frac{E-E_{(\mathrm{cal.})}}{0.000198322T}$$

Where E=observed potential difference in volts between the hydrogen and calomel half cells, with sign equal to that of the calomel half cell at potentiometric balance.

$E_{(\mathrm{cal.})}$=potential of calomel half cell at t centigrade (table 2).

T=absolute temperature ($273.1+t$ centigrade, observed). Values (*33*) for $0.000198322T$ from 10° to 40° C. are given in table 4.

Equation (1) is for the hydrogen electrode under a partial pressure of hydrogen of one atmosphere. For very exact measurements an E.M.F. correction should be applied for pressures other than one atmosphere; however, since this correction is very small for ordinary barometric fluctuations it may be ignored for soils and equation (1) used. The equation including the barometric correction $E_{(\mathrm{bar.})}$ is as follows:

$$(2) \qquad \mathrm{pH}=\frac{E+E_{(\mathrm{bar.})}-E_{(\mathrm{cal.})}}{0.000198322T}$$

$$\text{Where } E_{(\mathrm{bar.})} \text{ in volts } =\frac{0.000198322T}{2}\log\frac{760}{P_{H_2}}$$

P_{H_2}=partial pressure of hydrogen in mm.

The partial pressure of hydrogen P_{H_2} is that of the barometer minus the vapor pressure of the solution, the vapor pressure of the solution being assumed to be that of pure water at the observed temperature.

TABLE 4.—*Values for* $0.000198322T$

Temperature	$0.000198322T$	Temperature	$0.000198322T$
°C.		°C.	
10	0.056145	26	0.059318
11	.056343	27	.059516
12	.056542	28	.059715
13	.056740	29	.059913
14	.056938	30	.060111
15	.057137	31	.060310
16	.057335	32	.060508
17	.057533	33	.060706
18	.057732	34	.060905
19	.057930	35	.061103
20	.058128	36	.061301
21	.058327	37	.061500
22	.058525	38	.061698
23	.058723	39	.061896
24	.058921	40	.062095
25	.059120		

QUINHYDRONE-ELECTRODE METHOD

Since the development of the quinhydrone electrode for practical use and its adaptation to soils by Biilmann (*17*) the use of this electrode has become quite extensive by virtue of the fact that coating of the electrode and the use of hydrogen as in the hydrogen-electrode method are dispensed with and also because of its comparative simplicity and economy of time. The method is based upon the use of quinhydrone, a compound of one molecule of quinone with one molecule of hydroquinone, the former the oxidation product of the latter. In aqueous solution quinhydrone is dissociated into its equimolecular components, quinone and hydroquinone which are in equilibrium with each other. The quinhydrone-electrode equation may be derived from the electrochemical point of view representing the equilibrium as follows:

(3) $$C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + 2H^+ + 2\theta$$

Hydroquinone Quinone

or the electrode may be considered as a hydrogen electrode under a very low partial pressure of hydrogen, Biilmann (*15*, *16*) representing the equilibrium as follows:

(4) $$C_6H_4(OH)_2 \rightleftarrows C_6H_4O_2 + H_2$$

Since quinhydrone yields equimolecular quantities of quinone and hydroquinone, the ratio quinone to hydroquinone is unity and this term vanishes from the equation so the potential changes with changes in hydrogen-ion concentration as does the hydrogen electrode. The detailed derivation of the equation has been previously given. (*16*, *33*, *72*, *78*). Briefly the method consists in adding a small quantity of quinhydrone to the soil suspension, shaking the mixture, then inserting a platinum or gold electrode and measuring the potential against a standard half cell, from which potential and observed temperature the pH value is calculated.

Some investigators have reported excellent results with the quinhydrone electrode while others have been unable to obtain stable and reproducible potentials and have found their results in many cases to be in error. Christensen and Jensen's (*30*) results on many diverse Danish soils from pH 3.5 to 8.5 showed close agreement between the quinhydrone and hydrogen electrodes. Baver (*9*) showed that the hydrogen and quinhydrone electrode results compare closely, the variations ranging from 0 to 0.2 pH. Biilmann and Jensen (*20*) reported excellent agreement between the hydrogen and quinhydrone electrodes, the agreement in most cases being within 0.1 pH. While the results obtained by the writer (*96*) on soils from about pH 4 to 9.2 by the hydrogen and quinhydrone electrodes showed fair agreement in most cases, and in one instance as high as pH 9.2, there were, however, occasional wide discrepancies on the acid and alkaline sides, the larger discrepancies being more frequent on the alkaline side.

Brioux and Pien (*27*), were unable to obtain in general the agreement between the two electrodes as reported by Christensen and Jensen (*30*). Kühn (*70*) concluded that the soil investigator should give up the not-altogether-precise quinhydrone method and use the

indicator method. From the results by Olsen and Linderstrøm-Lang (*83*) the quinhydrone electrode on soil suspensions in some cases gave a pH value as much as 0.8 too high. The cases in question did not appear to be limited to any particular range of pH values, or to soils or localities of any particular character. In a communication from W. H. Pierre, then with the Alabama Polytechnic Institute, it was stated that a number of soils, by the quinhydrone electrode, gave pH values 0.5 to 1.0 higher than did the hydrogen-electrode or colorimetric methods. When the quinhydrone electrode was applied to soil extracts instead of soil suspensions good agreement with the other two methods was obtained.

Because of the discrepancies observed with the quinhydrone electrode, the International Society of Soil Science appointed a committee to study the quinhydrone electrode. It was conclusively shown (*94*) that many soils gave much higher equilibrium pH values by the quinhydrone electrode than by other methods and that these soils are the ones which show a rapid increase in pH within the first few seconds after the addition of quinhydrone.

LIMITATIONS OF THE QUINHYDRONE ELECTRODE

The quinhydrone electrode, because of various interfering factors is inapplicable to soils above about pH 8.5 and to soils containing manganese in a highly oxidized state, mainly as the dioxide. An important factor bearing upon the pH limitation of the quinhydrone electrode is the ionization of hydroquinone as a weak dibasic acid and the effect on the acid-base equilibria. In addition a variation in the ratio of quinone to hydroquinone may cause an error. It is essential that the ratio between quinone and hydroquinone be maintained equal to unity. The factors which may alter this ratio between oxidant and reductant and become of importance in alkaline solutions are the ionization of hydroquinone as a weak acid and the oxidation or reduction of hydroquinone or quinone by other active oxidizing or reducing agents. For a saturated aqueous solution of quinhydrone Kolthoff and Bosch (*67*) calculated the pH value to be 5.85. In regard to the acidity affect of hydroquinone Best (*13*) used the quinhydrone electrode (quinhydrone prepared according to Valeur (*102*)) in totally unbuffered solutions of pH value 1 to 5, but obtained erroneous results in such solutions with a pH value greater than 5. In the titration of poorly buffered solutions of weak acids Rabinowitsch and Kargin (*88*) found that above about pH 6 the quinhydrone electrode gave lower values than the hydrogen electrode. Kolthoff and Bosch (*67*) show that the hydrogen and quinhydrone electrodes are in good agreement in poorly buffered solutions of pH value less than about 7 provided that the quinhydrone is free from acid-oxidation products. Quinhydrone prepared according to Valeur (*102*) is especially recommended for poorly buffered solutions since it is quite stable and even after prolonged standing scarcely becomes perceptibly acid. Kolthoff and Bosch (*67*) state that quinhydrone prepared from hydroquinone and iron alum (*22*) and washed free from acid, again oxidizes slightly upon prolonged storage with the formation of acid-oxidation products. Such preparations show in poorly buffered solutions a much too acid reaction; however, if carefully washed before use good results may be obtained below pH 7. With solutions not too

slightly buffered excellent results are obtained with quinhydrone prepared by different methods.

In buffered solutions, more acid than pH 8, La Mer and Parsons (*72*) obtained reliable results with the quinhydrone electrode provided no rapid oxidizing or reducing agents were present. Kolthoff (*66*) states that if the buffer action of the solution is large enough (Clark's 0.05 M buffer mixtures used) good agreement between the hydrogen and quinhydrone electrodes may be obtained up to pH 9.0 if the quinhydrone-electrode measurement is made quickly after the addition of quinhydrone.

The autoxidation of hydroquinone by the oxygen of the air and the effect of the acidity of hydroquinone on the actual pH in unbuffered alkaline solutions (*72*) are important factors in yielding erroneous results in alkaline solutions. La Mer and Rideal's results (*73*) on the rate at which hydroquinone reacts with molecular oxygen show that the rate does not become appreciable until the solution (borate buffer) is more alkaline than pH 7.3 and that a comparable rate with air is not reached until about pH 7.8. It should be possible to avoid in large measure the complication of autoxidation (*72*) for rough titration work by working rapidly (above pH 8.0) and avoiding undue shaking in air. In regard to oxidizing agents it is interesting to note that Biilmann (*18*) obtained practically constant potentials over a period of many hours with the quinhydrone electrode in solutions of 0.1 normal hydrochloric acid, nitric acid, and mixtures of these acids. It is hardly probable, therefore, that the presence of nitrates in soils would interfere with the quinhydrone electrode. While occasionally the quinhydrone electrode has shown agreement with the hydrogen electrode on well-buffered soils as high as about pH 9.0 (*14*, *96*) it is advisable to limit the quinhydrone electrode to soils below about pH 8.5.

Another interfering factor in the use of the quinhydrone electrode is the presence of manganese. In this connection McGeorge (*77*) concluded from a study of Hawaiian soils that the accuracy of the quinhydrone electrode for the determination of the pH value of soils is greatly affected by the presence of small amounts of manganese dioxide. It is further stated that the potential drift with manganiferous soils is sufficiently rapid and characteristic as to warn the analyst against reporting erroneous results on such types. Discrepancies with the quinhydrone electrode were also observed by Heintze and Crowther (*56*) on some soils from west Africa, Siam, and England, the quinhydrone electrode results frequently being 1.0 pH higher than the hydrogen-electrode results. The reduction of acidity in certain soils was attributed by Heintze and Crowther to the presence of an active form of manganese dioxide in intimate association with the soil colloids, the manganese dioxide being reduced by hydroquinone to manganese hydroxide which neutralizes a portion of the soil acids. Discrepancies attributed to manganese have also been reported by others. (*6*, *14*, *63*, *69*).

In regard to the potential drift not infrequently observed with the quinhydrone electrode this may be so rapid that unless the potential is read immediately after adding the quinhydrone this drift may not be detected, and steady and reproducible values may be observed at later intervals and yet be in error. Obviously the quinhydrone-electrode procedure should be such as to favor the easy detection of

any potential drifts. In the use of the quinhydrone electrode a decided potential drift during the first minute immediately after the addition of the quinhydrone should be looked upon with suspicion. Best (*14*) calls attention to a form of potential drift which he termed an "adaptation lag." When a determination was made on a soil B immediately after having used the electrode in a soil A of different pH value, the electrode having been washed, there was a potential drift towards the equilibrium value, beginning on the side nearer A. The equilibrium value obtained after the drift was the same as that determined with a fresh electrode and agreed with the hydrogen-electrode value. This adaptation lag is eliminated entirely in most cases by placing the electrode only in the suspension for 1 minute, then removing the electrode and washing, adding the quinhydrone and replacing the electrode. The remainder of the procedure is similar to that described for the quinhydrone electrode.

QUINHYDRONE-ELECTRODE PROCEDURE

The International Society of Soil Science, as a result of their investigation (*94*) of the quinhydrone electrode, concluded that it is necessary to make a preliminary measurement in order to determine the suitability of a soil for the quinhydrone electrode. The preliminary procedure modified by the writer as regards the preparation of the soil suspension, is as follows:

A soil-water ratio of 1 to 2 is used and the mixture shaken in a Pyrex test tube for 1 minute and allowed to stand about 20 minutes. The quinhydrone is added (about 0.15 g of quinhydrone for a soil-water mixture containing 15 g of water) and the mixture immediately shaken vigorously for not more than 2 seconds. The uncoated platinum electrode (not smaller than 5 by 13 mm) and the potassium chloride bridge connecting the standard half cell are washed and inserted into the test tube so that the electrode is immersed in the settled soil and the potassium chloride bridge is in the upper region of the supernatant liquid. The potential is measured 10 (or at most 15) 30, and 60 seconds from the time of adding the quinhydrone. Where the increase in apparent pH value from 10 to 60 seconds in the preliminary measurement is less than 0.2 the soil may be regarded as suitable for the quinhydrone-electrode method, but the determination should be repeated less rapidly as follows:

The soil and water are shaken for 1 minute, as in the preliminary measurement, but after the addition of the quinhydrone, the mixture is shaken for 10 seconds and the potential measured 60 seconds after adding the quinhydrone.

Where the increase in apparent pH value from 10 to 60 seconds in the preliminary measurement is more than 0.2, the soil is unsuitable for the quinhydrone-electrode method and it is better to use some other method. In this case an approximate pH value may be obtained if the preliminary measurement is repeated on a new sample and the reading taken at 10 seconds. Such approximate values should be recorded as "10-second values."

QUINHYDRONE-ELECTRODE EQUATIONS FOR CALCULATING pH VALUE

The potential-temperature curve of the quinhydrone electrode over the range 0°, 18°, 25°, and 37° C., respectively, was determined by

Biilmann and coworkers (*18, 21, 22*) and is represented by the following equation:

$$\pi_t = 0.7175 - 0.00074t \tag{5}$$

In equation (1) E is replaced by $\pi_t - E_q$ and the quinhydrone-electrode equation for calculating the pH value when using a standard calomel half cell is:

$$\text{pH} = \frac{\pi_t - E_{(\text{cal.})} - E_q}{0.000198322T} \tag{6}$$

Where $\pi_t = 0.7175 - 0.00074t$

t = ° C., observed.

E_q = observed potential difference in volts between the quinhydrone and calomel half cells, with sign equal to that of the quinhydrone half cell at potentiometric balance.

$E_{(\text{cal.})}$ and T = as in equation (1).

When using a standard calomel half cell there is a current reversal and change in sign of the observed potential at a definite pH value depending on the half cell used and on the temperature. From equation (6) it is seen that with the 0.1N calomel half cell at 18° the potential is zero at pH 6.34 and above this the potential is negative. Using the saturated calomel half cell at 18° the observed potential is zero at pH 7.85, below pH 7.85 the observed potential will be positive, since the quinhydrone electrode is positive to the calomel electrode and above pH 7.85 the observed potential is negative. It is advisable to insert a properly wired double-throw switch in the circuit for reversing the polarity. The polarity of an unknown cell may be easily ascertained by observing which electrode has to be connected to the positive terminal of the potentiometer in order to balance the potentiometer against the unknown E.M.F. since a balance cannot be obtained unless the unknown cell is properly connected to the potentiometer so that the E.M.F.'s are in opposition, plus to plus and minus to minus.

The quinhydrone electrode equation, using a Veibel standard half cell (previously described) is as follows:

$$\text{pH} = 2.03 + \frac{E_q}{0.000198322\ T} \tag{7}$$

where E_q is the observed potential difference in volts between the soil as a quinhydrone half cell and the standard half cell. The sign of the observed potential is that of the standard half cell at potentiometric balance. For pH values above 2.03 the observed potential is positive, for pH values equal to 2.03 the potential is zero, and for pH values below 2.03 the polarity reverses and the observed potential is negative.

ANTIMONY-ELECTRODE METHOD

The antimony electrode was employed by Uhl and Kestranek (*101*) for analytical neutralizations, and later an extensive study of its properties was made by Kolthoff and Hartong (*68*). Later Franke and Willaman (*43*) made a study of the antimony electrode and applied it to the determination of the pH value of paper-mill liquors. The writer applied the antimony electrode to the determination of the pH

value of soils (*97*) from pH 3.6 to 9.2 and found good agreement with the hydrogen electrode. It has subsequently been applied to soils by other investigators (*7, 14, 45, 51, 74*). Since the use of the antimony electrode eliminates the necessity for plating electrodes and the use of hydrogen or quinhydrone, the determination of the pH value of soils by this electrode is simplified and expedited as compared to the customary electrometric procedures.

Briefly, the method consists in placing an antimony electrode in the soil suspension and measuring the potential of this half cell against a standard half cell.

Some investigators have measured the potential during shaking (*61, 74, 97*) while others have measured it with the vessel at rest (*45*) that is, after having stirred the suspension with the stick antimony electrode (*7, 14, 51*) with or without the addition of Sb_2O_3.

PREPARATION OF THE ANTIMONY ELECTRODE

Kolthoff and Hartong (*68*) used for their electrode antimony analyzing 99.97 percent antimony, which was melted and poured into a rodlike mold. These investigators obtained more reliable results and constant potentials more rapidly when a little antimony trioxide was added to the solution. According to Uhl and Kestranek (*101*) whose results Kolthoff and Hartong also confirmed, the antimony contains sufficient oxide so that any further addition is unnecessary. Franke and Willaman (*43*) obtained the best electrodes from ordinary pure stick antimony by pouring the molten antimony into a Pyrex tube sealed at one end and embedded in a heated sand bath. For the determination of the pH value of soils the writer has used stick antimony purchased as chemically pure and measuring about 7 mm in diameter, which was cut into 4-cm lengths. Many electrodes were used as such and also recast from this antimony, while a number of electrodes were also cast from antimony analyzing Sb, 99.94 percent; Pb, 0.05 percent; Fe, 0.013 percent; Cu, none; Sn, none; Zn, none; and As, a trace. Some electrodes were made by melting the antimony in a vertical Pyrex tube sealed at one end and gradually cooled, while others were made by pouring the molten metal into the Pyrex tube embedded in a heated sand bath, permitting gradual cooling. The electrodes, which were of different lengths, were filed smooth and polished on a buffing wheel and then washed. They took on a very bright finish but gradually oxidized in the air. Franke and Willaman (*43*) state that a bright electrode no doubt gives a quicker response than a tarnished one but shows more tendency for a potential drift and consequently they recommend a tarnished electrode. Electrical connection was made to the electrodes by soldering one end to a copper wire. The wire and about 1 cm of the electrode were inserted into a Pyrex tube and the electrode held in place with De Khotinsky cement. Lava and Hemedes (*74*) prepared stick electrodes from Kahlbaum antimony powder, pouring the molten metal into a tube heated on a sand bath, preventing sudden cooling. Harrison and Vridhachalam (*51*) state that a much quicker and sharper equilibrium was attained with extra pure antimony, the electrodes being cast in vertical molds in order to obtain uniform crystallization. The electrodes were filed, then smoothed with emery paper and polished with the finest carborundum powder and water. Harrison and Vridhachalam (*51*) recommend keeping the electrode bright and

clean by dipping it into aqua regia for a few seconds, washing quickly in water and polishing with a damp soft cloth. They state tarnished electrodes are less sensitive. Parks and Beard (*84*) used electrodes (made from chemically pure analyzed antimony) which were cooled very slowly in a temperature-controlled furnace (large crystals) and electrodes which were allowed to cool normally to room temperature (fine crystals) then polished bright and clean with fine emery cloth and rinsed in distilled water before using. The greatest deviation of the antimony electrode from the hydrogen electrode between pH 1.6 and 7.8 was ± 0.05 pH and between pH 2.2 and 7.0 inclusive ± 0.02 pH. Uemura and Sueda (*100*) suddenly cooled their electrodes by plunging the tube of fused antimony into water. These authors state that the mechanical treatment of the electrodes such as polishing with emery paper has little influence on the E.M.F., but the original minute impurities and porousness of the electrode cannot be neglected. From the foregoing it is clear that there is little uniformity in the method of preparing the stick antimony electrode.

Roberts and Fenwick (*89*) used, instead of stick antimony electrodes, crystals of the metal and oxide. As the oxide, cubic crystals of Sb_2O_3 were used and were obtained by heating the precipitated oxide at 470° C. for 24 hours.

ANTIMONY-ELECTRODE PROCEDURE

The antimony-electrode procedure for soils followed by the writer is as follows: The soil treatment and filling of the electrode vessel (fig. 3) are as described for the hydrogen-electrode procedure. The stick antimony electrode is well washed with distilled water, inserted in a rubber stopper, and placed in the vessel (fig. 1). The vessel is shaken about 1 or 2 minutes, liquid junction with the standard half cell made as described for the hydrogen-electrode procedure, and the potential read during shaking. In most instances the potential read after bringing the vessel to rest drifted rapidly. The potentials which were measured against a saturated calomel half cell were corrected to the N/1 calomel half cell and the pH values calculated (*97*) from the equation of Franke and Willaman (table 5). The sign of the observed potential was that of the calomel half cell which is positive to the antimony half cell at potentiometric balance.

With poorly buffered solutions Best (*14*) found it necessary to add Sb_2O_3 in order to obtain steady values, and consequently suggests its addition to all soils. His procedure consists in adding Sb_2O_3 (enough to cover a 4-mm diameter disk) to about 15 ml of the suspension in a test tube. After shaking the suspension it was stirred with the stick antimony electrode. After 1 minute the electrode was removed, washed with distilled water, and excess water removed by lightly touching with a piece of filter paper. The electrode was replaced and the potential read within one-half minute and at intervals of one-half minute, the equilibrium being approached from the alkaline side as stipulated by Roberts and Fenwick (*89*). If the potential drift after the first reading did not amount to more than 1 millivolt per minute, the first reading was recorded. The determination was repeated if the drift was more rapid. The pH value was read from a calibration curve. A lag in the attainment of equilibrium similar to the adaptation lag of the quinhydrone electrode was observed with the antimony

electrode and because of this the soil was first stirred with the electrode to be used.

ANTIMONY-ELECTRODE EQUATIONS FOR CALCULATING pH VALUE

The equation for the antimony-antimony trioxide electrode (*89*) at 25° C. is as follows:

$$(8) \qquad E=E_o+0.05915\ [\mathrm{pH}-\tfrac{1}{6}\log\ (Sb_2O_3)+\tfrac{1}{2}\log\ (H_2O)]$$

Disregarding the last two terms, equation (8) reduces to

$$(9) \qquad E=E_o+0.05915\ \mathrm{pH}$$

Roberts and Fenwick (*89*) state that in equation (8) the term involving the activity of water may be neglected and the term involving the activity of the solid oxide disappears if the oxide is in the stable crystalline form (cubic Sb_2O_3), a condition which must hold if the electrode is to attain its highest accuracy. For the constant E_o these authors obtained the value -0.1445 volts at 25° C., so equation (9) becomes

$$(10) \qquad E=-0.1445+0.05915\ \mathrm{pH}$$

where E=potential difference between the antimony-antimony trioxide half cell and the standard normal hydrogen half cell the sign of the potential being that of the standard half cell at potentiometric balance.

$0.05915=0.000198322T$ (equation 1) when $t=25°$ C.
pH=that of the solution of the antimony-antimony trioxide half cell.

Roberts' and Fenwick's electrode, in contrast to the stick electrodes of other workers, consisted of crystals of the metal and oxide in a vessel adapted to solutions rather than to soils. The maximum accuracy was attained with cubic oxide (the presence of any unstable solid phase notably orthorhombic Sb_2O_3 being avoided), the elimination of dissolved oxygen from the solution by using nitrogen as a gas phase, and approaching equilibrium from the alkaline side, that is, using in the preceding determination a solution more alkaline than the one being studied. Under these conditions the potential is a linear function of the pH of the solution, with the theoretical slope (0.05915) from pH 1 to 10. Roberts and Fenwick found that their results in air so closely approached those in nitrogen in regard to the magnitude of the deviations from linearity that the antimony electrode in air may be recommended for general use provided the value of E_o is fixed by means of two or more buffer solutions of known pH in the range desired. These authors state that the pH value obtained after 30 minutes is generally within 0.1 pH of the equilibrium value and since the error is always on the acid side the true pH can probably be estimated to within 0.05 pH. For an accuracy of 0.01 pH or greater 24 hours may be required.

Equations derived by other investigators and recalculated to apply to the N/1 calomel half cell, are shown in table 5 where E is the potential difference between the antimony-antimony trioxide half cell and the N/1 calomel half cell, the sign of the observed potential being that of the standard half cell at potentiometric balance.

TABLE 5.—*Equations for the stick antimony electrode with a N/1 calomel half cell*

Investigators	Equation	Temperature
		°C.
Kolthoff and Hartong	$E = 0.0415 + 0.0485$ pH (pH 1 to 5)	14
Do	$E = .009 + .0536$ pH (pH above 9)	14
Franke and Willaman	$E = .050 + .054$ pH (pH 1 to 12)	25
Lava and Hemedes	$E = .052 + .057$ pH	26–29
Harrison and Vridhachalam	$E = .0649 + .0498$ pH (pH 4 to 9)	30
Best	$E = .0549 + .0526$ pH (pH 8 to 10)	27
Do	$E = .0532 + .0510$ pH (pH 8 to 10)	20
Do	$E = .0615 + .0476$ pH (pH 8 to 10)	14
Do	$E = .0512 + .0549$ pH (pH 5 to 7)	27
Do	$E = .0430 + .0513$ pH (pH 5 to 7)	14
Parks and Beard	$E = .030 + .05915$ pH (pH 2 to 7)	25

Because of the variation in the preparation of the stick antimony electrodes and in the procedure followed by different investigators the equations in table 5 show poor agreement. When the requirements for the maximum accuracy of the antimony-antimony trioxide electrode as given by Roberts and Fenwick (*89*) do not prevail it is necessary that the electrode be calibrated for the conditions under which it is to be used. The potential difference between the antimony electrode, in buffer solutions of known pH, and a standard half cell may be determined for the pH range and temperature desired. Curves for the particular temperatures may then be drawn by plotting the observed potential against the pH value of the buffers. The pH value of the unknown corresponding to the observed potential may then be read from the calibration curve.

COLORIMETRIC METHOD

The colorimetric method for the determination of the pH value depends on the fact that an indicator exhibits a gradual color change within a characteristic pH range. Above and below this range a characteristic color appears (for a two-colored indicator) and within the range the color may be considered as a mixture of the two characteristic colors. The pH value corresponding to the point where the indicator is half transformed (mid-point of the range) is designated the pK value (table 7) for the indicator below which value the "acid color" of the indicator appears and above which the "alkaline color" appears, acid and alkaline here referring to the acid and alkaline forms of the indicator rather than to pH 7 as an orienting value.

In the colorimetric determination of pH values the standard solutions used are termed "buffer solutions" which are generally mixtures of some acid and its alkali salt, the pH value of which has been accurately determined by the hydrogen electrode. The pH value of the solution under investigation is determined by comparing this solution, plus indicator, with these buffer solutions containing the same indicator of the same concentration. The term "buffer action" may be defined as the resistance offered by a solution to a variation in its pH value as a result of the addition or loss of acid or alkali. A detailed discussion of indicators and buffer solutions has been given (*33*) so its repetition is unnecessary. As many colorimetric methods are to be found in the literature, reference will be made to only a few which embody different principles.

The double-wedge principle of Bjerrum (*24*) consists of two wedges, one containing the indicator in the acid form and the other containing it in the alkaline form. A view through these wedges should give the intermediate colors of the indicator. An attached scale gives the pH values for the corresponding colors with which the unknown is compared.

A set developed by Morgan (*80*) for use in the field or laboratory consists of a small porcelain block with a depression near the top of its sloping surface, divided into two parts separated by means of a perforated wall. From the lower part of this depression a channel runs to the bottom of the sloping surface, ending in another depression. The lower part of the upper depression is filled with soil, and indicator solution added. After passing through the soil and into the depression at the bottom, the solution is compared with a printed color chart. Some difficulty, however, has been experienced in matching the color of the unknown, due in part to its turbidity and to the fading of the printed color standards.

Gadd (*44*) described a method for the determination of the pH values of turbid soil and other solutions, the basic principle of which was previously used by Atkins (*4*). Two parts of water and one of air-dried soil are shaken in a vessel for 10 minutes and allowed to stand for 24 hours. About 3 ml of the indicator solutions recommended by Clark (*33*) are required for 25 ml of the soil solution. If the solution is very turbid the amount of indicator may be doubled. Equal quantities (about 5 ml) of the colored samples are placed in uniform tubes and 10 drops of distilled water are added to one of the tubes, used as a control. Ten drops of a known buffer solution are added to another tube, and the resulting color is compared with that of the control. If no alteration in color occurs, the soil solution and buffer have the same pH; if there is a color change, other buffer solutions are tried. If one buffer is too acid and the other too alkaline, then the pH may be estimated by interpolation. If the turbidity of the soil solution is such as to make it difficult to determine which buffer has caused the least alteration in color, the control and buffered tubes in question may be diluted with equal quantities of distilled water and again compared.

Gillespie (*48*) described a colorimeter for the determination of hydrogen-ion concentrations, consisting of 3 concentric vessels on one side and 2 on the other. Of the three vessels the middle movable one contains the acid form and the lower one the alkaline form of the indicator. The position of the center vessel determines the ratio of the acid and alkaline forms of the indicator. The top tube may be used for turbidity compensation. Of the two vessels on the other side the lower one contains the unknown with indicator. The writer applied Gillespie's principle to the Duboscq colorimeter for the determination of pH values and obtained excellent results. There is now available a combination standard and pH colorimeter similar in principle to Gillespie's and having an electric lamp and daylight filter in the base of the instrument with an illuminated table for the calculation of results.

A different type comparator is one consisting of a wooden drum holding buffer solutions and revolving inside of a metal band. A block holding three test tubes is fastened to the front of the band,

and by the aid of an electric lamp and a daylight glass comparisons are made by revolving the drum.

Another form of comparator consists of a small revolving disk for each indicator and holding smaller color disks corresponding to the range of the particular indicator.

The drop-ratio method of Gillespie (*47*) eliminates the preparation of and electrometric standardization of buffer solutions. As this method requires little preparation other than the indicator solutions it will be described later in detail.

When using the colorimetric procedure, turbidity and color of the extract are interfering factors which, together with the human element, eye differences, and eye fatigue, lend both difficulty and uncertainty to the colorimetric method.

OBTAINING THE SOIL EXTRACT

For obtaining the soil extract for colorimetric determinations, such methods as centrifuging, filtering through filter paper, Pasteur-Chamberland filters, flocculating agents, suction filters, and dialysis through collodion sacks have been used.

Using an electric centrifuge for clarifying soil extracts Gillespie and Hurst (*50*) found that the electrometric and colorimetric results on a large number of soils agreed within the experimental error. Atkins (*5*), using a centrifuge, obtained clear solutions for almost all soils, although a few remained slightly turbid. The use of the centrifuge, where possible, is recommended by Atkins. Results obtained by Pierre (*85*) show an increase of 0.25 pH, due to centrifuging a clear soil extract in an open test tube, but no change when it is centrifuged in a closed test tube. Working with filtered soil extracts, Gillespie and Hurst (*50*) observed that soil extracts filtered through filter paper were incorrect and variable, according to the brand and treatment of the paper. Barnette, Hissink, and Van der Spek (*8*) found that filtrates (obtained through paper and "bougies") of suspensions of the four soils studied were acid, but always less acid than their corresponding suspensions. Atkins (*5*) concluded that the pH values of some soil extracts are markedly modified by filtration, even when a first filtrate is rejected. The acidity may be reduced by both untreated and acid-extracted filter papers. It was observed by Atkins that the rejection of a large first filtrate, about 160 ml, lessened the error resulting from filtration. Nehring (*82*) compared the pH determinations of soils made on suspensions (quinhydrone electrode) and filtrates and found widely deviating results by the use of different filter papers. Accordingly, Nehring states that the use of filtrates should be avoided. However, if filter paper must be used, only quantitative filter paper which has been repeatedly washed with boiled distilled water should be employed. Results obtained by the writer with Pasteur-Chamberland filters showed an increase in acidity with four alkaline soils as a result of filtering. These results are in agreement with those obtained by Fisher (*42*), who observed that soil extracts filtered through paper or Pasteur-Chamberland thimbles became more acid as filtration proceeded. Pierre and Parker (*87*) used a Pasteur-Chamberland filter and found a change in pH from 4.7 to 5.7 on one soil and no change on another. Gillespie (*47*), using colloidal iron for the clarification of soil extracts, found that the

extracts so obtained (from nine acid soils) gave the same results as were obtained by the usual methods, but he did not feel justified in recommending this procedure on the basis that other soils with probably less buffer action might possibly be changed by the residual acidity of the colloidal iron used. Kühn (*71*) used a special grade of barium sulphate (X-ray purity) as a clarifying agent, for soil suspensions. Using Kühn's method Baver and Rehling (*11*) found very satisfactory agreement between the colorimetric results on soil extracts obtained by this method and the collodion bag method and the electrometric results by the hydrogen electrode. In regard to Kühn's method the committee on soil reaction measurements of the International Society of Soil Science reported (*94*) that they have found the method of Kühn for clearing the suspension very useful and recommend its trial in other laboratories. Using a modified suction apparatus as devised by Truog (*99*), Pierre and Parker (*87*) found that the colorimetric results on these filtered soil extracts, collodion sack extracts, and the electrometric results on soil suspensions agree well. The filter paper was washed 10 or 15 times with hot conductivity water, was dried at 50° C., and stored in a desiccator. Regarding the use of collodion sacks, Pierre and Parker (*87*) conclude that this method of obtaining soil extracts is short, simple, and gives the soil extract in an unaltered condition.

DROP-RATIO METHOD

The drop-ratio method of Gillespie (*47*) consists in the comparison of the soil extract containing a definite quantity of indicator with pairs of standards, each pair containing 10 drops of the same indicator, which is distributed in the tubes in the ratio of 1 drop in one and 9 in the other, 2 to 8, 3 to 7, and so on to 9 to 1. The indicator in the front row of tubes is transformed to its alkaline color, and in the other row it is transformed to its acid color. The experimental standardization of the method and the theoretical equation for an indicator acting as a monobasic acid, relating the hydrogen-ion exponent and drop ratio, have been previously described by Gillespie (*47*). Gillespie states (*47, pp. 115–116*):

> The method should be of especial use in orienting experiments, or in occasional experiments involving hydrogen-ion exponent measurements, either where it is unnecessary to push to the highest degree of precision obtainable, or where the investigator may be content to carry out his measurements to his limit of precision and to record his results in such a form that they may be more closely interpreted when a more precise study of the indicators shall have been completed.

PREPARATION OF INDICATOR SOLUTIONS

In table 6 are given the percentage strengths of the various indicator solutions in terms of the free-acid indicator, together with the quantities of alkali used (in slight excess) to form the monosodium salts.

TABLE 6.—*Data for the determination of the hydrogen-ion exponent by the drop-ratio method*

Drop ratio	Hydrogen-ion exponent for each pair of tubes						
	Brom-phenol blue	Brom cresol green	Brom cresol purple	Brom thymol blue	Phenol red	Cresol red	Thymol blue
1 to 9	3.1	3.7	5.3	6.15	6.75	7.15	7.85
1.5 to 8.5	3.3	3.9	5.5	6.35	6.95	7.35	8.05
2 to 8	3.5	4.1	5.7	6.5	7.1	7.5	8.2
3 to 7	3.7	4.3	5.9	6.7	7.3	7.7	8.4
4 to 6	3.9	4.5	6.1	6.9	7.5	7.9	8.6
5 to 5	4.1	4.7	6.3	7.1	7.7	8.1	8.8
6 to 4	4.3	4.9	6.5	7.3	7.9	8.3	9.0
7 to 3	4.5	5.1	6.7	7.5	8.1	8.5	9.2
8 to 2	4.7	5.3	6.9	7.7	8.3	8.7	9.4
8.5 to 1.5	4.8	5.4	7.0	7.85	8.45	8.85	9.55
9 to 1	5.0	5.6	7.2	8.05	8.65	9.05	9.75
Amount in indicator solution—percent	0.008	0.015	0.012	0.008	0.004	0.008	0.008
0.1 N NaOH per 0.1 gram portion—ml	1.64	1.58	2.78	1.77	3.10	2.88	2.38
Produce acid color with	0.05N HCl 1 ml	0.05N HCl 1 drop	0.05N HCl 1 drop	0.05N HCl 1 drop	0.05N HCl 1 drop	2 percent KH_2PO_4 1 drop	2 percent KH_2PO_4 1 drop
Produce alkaline color with 0.05 N NaOH	1 drop	1 drop	1 drop	1 drop	1 drop	1 drop	2 drops

The weighed amount of the indicator is ground in an agate mortar (avoid a glass mortar) (*85*) with the standard alkali then made up to volume with distilled water and stored in Pyrex bottles. The standard alkali is given in 1.1 equivalents for all indicators except bromcresol purple, in which case 1.5 equivalents are used. Bromcresol green (*34, 60*) has been substituted in place of methyl red used by Gillespie (*47*). This indicator, being more stable than methyl red, which is easily reduced, completes a series of sulphonphthalein indicators.

Birge and Acree (*23, p. 1037, note 1*) state that by titrating the solutions of the monobasic salts of the sulphonphthalein indicators with more alkali and so adjusting the indicator solutions to any desired pH value it is possible to mix the indicator with a solution known to have approximately the same pH value and thereby obviate any appreciable change of the pH, even when the solution has weak buffer properties. According to Atkins (*5*) the indicators should be used in their half-transformed condition, this being of particular importance when dealing with lightly buffered soil extracts or natural waters. Pierre and Fudge (*86*) state that in order to obtain accurate results with slightly buffered soil extracts or unbuffered solutions of any kind, the pH values of the indicator solutions should be adjusted so as to correspond to a pH value near the middle of the transition interval of the indicator.

For the colorimetric determination of the pH value of soils the indicators should at least be adjusted to their respective mid-points (pK value table 7). This may be done easily as described under isohydric indicators. Most soil extracts are little affected by the indicator solutions adjusted to their mid-points, however, for very precise work, and when testing very weakly buffered solutions isohydric indicator solutions should be used.

TABLE 7.—*Indicator characteristics*

[From Clark]

Name	Molecular weight	pK value	ml [1] NaOH
Bromphenol blue	669	3.98	14.9
Bromcresol green	698	4.67	14.3
Bromcresol purple	540	6.3	18.5
Chlorphenol red	423	5.98	23.6
Bromthymol blue	624	7.0	16.0
Phenol red	354	7.9	28.2
Cresol red	382	8.3	26.2
Thymol blue	466	[2] 8.9	21.5

[1] ml NaOH=ml of 0.01 N NaOH per 0.1 g indicator to form monosodium salt. Dilute to 250 ml for 0.04-percent solution.
[2] Alkaline range.

ISOHYDRIC INDICATORS, PREPARATION AND USE

In using the colorimetric method it is often assumed that the buffer capacity of the unknown solution is sufficiently great so as to be practically unaffected by the addition of the indicator. With very poorly buffered solutions, however, the pH value of the indicator solution is of importance and it becomes necessary to adjust the pH value of the indicator solution to the mid-point or use isohydric indicators; that is, having the same pH as the unknown.,

The isohydric indicator method is the use of an indicator solution made up to the same pH as the unknown in order to prevent the unknown and the indicator from changing each other and to give a final mixture at the same pH as the unknown. The preparation of isohydric indicators (*1*, *39*) is as follows: The indicator is dissolved by warming with one equivalent of alkali (table 7) preferably 0.05-N solution, and diluted to 0.04 percent, or better to 0.001 M, as desired. The stock solution was divided into several 100 ml portions in individual Pyrex flasks and adjusted as follows: As an example, take bromthymol blue covering the range pH 6 to 7.6. A volume such as 0.2 ml of one 100-ml portion was put into a Pyrex test tube and stoppered. Another 0.2 ml was put into a second Pyrex test tube to which was added 0.2 ml of a 0.001-M (or 0.2 ml of 0.05-M) buffer (air-equilibrated) (*40*) and having the electrometric pH value of 6.2 and the tube stoppered. This formed the first provisional micro buffer-color standard. The two test tubes were laid on their sides over white porcelain or paper and the colors compared through substantially equal areas. If the pH of the indicator solution was below or above the pH 6.2 micro buffer-color standard, the 100-ml portion of stock indicator was titrated with 0.05 N NaOH or HCl until 0.2-ml portion thereof exactly matched the color of another 0.2-ml portion thereof plus 0.2 ml of the pH 6.2 (0.001-M) buffer solution. This 100-ml portion of the indicator was then set aside as the standard pH 6.2 bromthymol blue solution. In order to adjust a second 100-ml portion of the stock indicator to pH 6.4, 0.2 ml each of the pH 6.2 indicator and a pH 6.4 (0.001-M) buffer were mixed. This made a second provisional micro buffer-color standard of approximately pH 6.4 against which 0.2-ml portions of the second 100 ml of stock indicator were compared after successive additions of 0.05-N alkali to bring its pH up to 6.4. When correctly adjusted the color of the indicator solution is not changed

by the addition of 0.2 ml of the 0.001-M buffer of the same rated pH, or pH 6.4 in this case. By this stepwise adjustment of the pH values of the several 100-ml portions of the 0.001-M stock-indicator solution and the use of the same with the 0.001-M buffers to form the corresponding accurate micro buffer-color standard, great precision is obtained. Acree and Fawcett (*1*) used what they termed "pH 7.0 water" in their preparation and study of isohydric-indicator solutions for certain purposes, but show that a good grade of distilled water is satisfactory for most practical purposes. The 0.001-M indicators should be stabilized against the action of atmospheric carbon dioxide by thorough aeration of the indicator solution during the pH adjustments (*39, 40*) so as to be in equilibrium with atmospheric carbon dioxide. A set of 0.001-M bromthymol-blue solutions (stabilized as previously mentioned) in Pyrex bottles equipped with small rubber bulbs on ground, hollow Pyrex stoppers sealed to graduated capillary tubes showed less than 0.1 pH change with moderate use for 1 year.

The isohydric indicators are used as follows: A small drop of the unknown is mixed with a drop of each indicator to find 1 or 2 indicators responding to the pH of the unknown. From 0.2 to 10 ml of the unknown solution are added to 0.2 ml of the proper indicator solution adjusted to its mid-point (pK value, table 7), such as pH 7.0 for bromthymol blue. The comparison of this solution against the 0.001-M (or 0.05-M) buffer-color pH standards with corresponding volumes gives an approximate pH reading for the unknown which is below, at, or above the mid-point pH of the indicator. It is then possible to use the approximate pH to formulate an estimated pH of the unknown. By mixing another sample of the unknown with 0.2 ml of that indicator solution having the estimated pH and matching it against the buffer-color standards, there will usually be exact or nearly exact agreement between the pH of the indicator used and the pH as read; thus a new correct, or nearly correct, pH reading is obtained. Electrometric and colorimetric data are given by Acree and Fawcett (*1*) showing the relation between the dilution of buffers and the salt and protein errors of the indicators used.

PREPARATION OF COLOR STANDARDS FOR THE DROP-RATIO METHOD

The test tubes used for the color standards are approximately 1.5 cm external diameter and 15 cm long, preferably without flanges. Sufficient uniform test tubes should be selected by pouring 10 ml of water into each and retaining those which are filled to the same heights or within a few millimeters. The test tubes may be weathered by boiling for one-half hour in chromic acid solution. Test-tube racks having two rows are used for holding the pairs of standards. To prepare a set of standards for any indicator 1 drop of the indicator is placed in the first test tube and 9 in the rear one, 2 in the second and 8 in the rear one and so on up to 9 in the last and 1 in the rear. In table 6 are given the quantities of alkali to be added to the front row of test tubes to develop the alkaline color and the quantities and type of acid to be added to the rear row to develop the acid color, the strengths being only approximate. The volume is now made up to a height corresponding to 5 ml. The 1.5 to 8.5 ratio, when needed, is prepared by using 3 and 17 drops, respectively. Before preparing a color standard 1-ml portions of the unknown should be tested with 2 drops of the different indicators. After having become familiar with

the color changes and useful ranges of the different indicators it is a comparatively simple matter to ascertain which indicator to employ in the preparation of the standards.

DROP-RATIO PROCEDURE

Having determined the indicator to be used and having prepared the color standards, 10 drops of the indicator are added to a test tube and sufficient of the centrifuged soil extract is added to bring the volume up to a height corresponding to 5 ml. The centrifugate is obtained by centrifuging for about 15 minutes at approximately 3,000 revolutions per minute, the supernatant liquid from 15 g of soil and 30 ml of water which have been shaken vigorously about 1 minute in a large rubber-stoppered Pyrex test tube and allowed to stand about 20 minutes, or longer, for sedimentation and to approach equilibrium. The test tube containing the centrifugate and indicator is placed in the comparator (fig. 6) and compared with different pairs of the color standards until its position relative to the color standards is located.

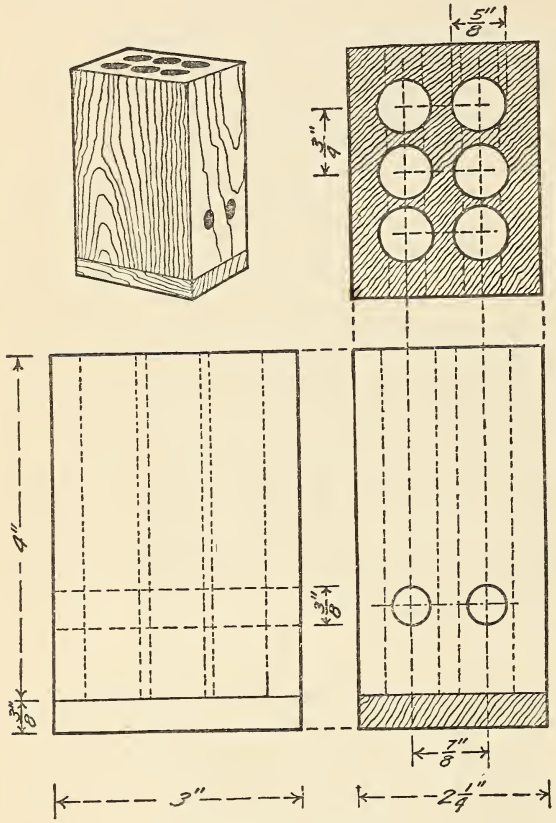

FIGURE 6.—The comparator.

The comparator shown in figure 6 is an adaptation of the principle of Walpole (*104*) and consists of a block of wood with 2 rows of holes with 3 in each row, through each row passing a smaller view hole. The test-tube holes, which should lie in the indicated planes and should be as close as possible, will accommodate test tubes a trifle smaller in external diameter than five-eighths of an inch. The interior is painted flat black. Considering the top view of the comparator 2 test tubes of water are placed in the 2 upper left-hand holes and the unknown with indicator in the lower left-hand hole. The test tube containing the unknown solution without indicator, to compensate for turbidity, is placed in the upper right-hand hole and the pair of color standards in the lower right-hand holes. The view should be made against the clear sky. It is essential to work within the ratios

1:9 and 9:1, since the percentage transformation of the indicators at these points is such that the hydrogen-ion exponent of the unknown may be different from that indicated by the ratio, without a color difference being present to show this. It may so happen that the color of the unknown does not match exactly a pair of standards, in which instance its intermediate position between two pairs of standards is located, and from table 6 the value of the hydrogen-ion exponent is read. If, when working with bromcresol purple, the dichromatism of the indicator becomes such a disturbing factor that it is difficult to obtain a match, the tubes may be viewed against a yellow light as suggested by Clark (*33*). Use is made of a box containing a carbon-filament electric light, the rays passing through tracing paper stained yellow by painting with a solution of 5 ml of a 0.6-percent solution of phenol red and 5 ml of M/5 KH_2PO_4. To avoid the dichromatism of bromcresol purple, bromphenol red or chlorphenol red (*34*) may be used advantageously, as their ranges are similar to that of bromcresol purple.

In a paper by Hatfield (*53*) a modification of Gillespie's method is offered in which buffer solutions are used for producing the acid and alkaline colors of the indicators. It is claimed that the color standards are more permanent under these conditions. In regard to the permanency of the color standards, Gillespie (*47*) states that it would appear that no change whatever need be feared during the first day, except possibly in the case of cresol red and thymol blue, this apparently being dependent on the laboratory atmosphere.

SUMMARY

The hydrogen-, quinhydrone-, and antimony-electrode methods, details of electrometric measurements, colorimetric methods, particularly Gillespie's drop-ratio method, isohydric indicators, and limitations of the electrometric methods are described.

Physicochemical acidity and the pH value, factors affecting the hydrogen-ion concentration of soils, such as the periodic variation of hydrogen-ion concentration, drying, grinding, the soil-water ratio, the quality of distilled water and the preparation of the soil sample are discussed along with other data essential in the determination of the hydrogen-ion concentration of soils.

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